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THE HARD START PHENOMENA IN HYPERGOLIC ENGINES

VOLUME IV. THE CHEMISTRY OF HYDRAZINE FUELS AND NITROGEN TETROXIDE PROPELLANT SYSTEMS

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by

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VOLUME IV. THE CHEMISTRY OF HYDRAZINE FUELS
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Yael Miron¹ and H. E. Perlee²

INTRODUCTION

This volume discusses the various chemical reactions that occur and that could possibly occur in the RCS engines utilizing hydrazine-type fuel/nitrogen tetroxide propellant systems, prior to ignition (preignition), during combustion, and after combustion (postcombustion), and endeavors to relate the "hard-start" phenomenon to some of these reactions. The discussion is based on studies conducted by Bureau investigators and others utilizing a variety of experimental techniques and apparatus as well as current theories of chemical reactions and reaction kinetics. The chemical reactions were studied in low pressure gas flow reactors, low temperature homogeneous- and heterogeneous-phase reactors, simulated two-dimensional (2-D) engines, and scaled and full size engines. Nonchemical causes also have been suggested and considered for the hard-start phenomenon; they are discussed in other volumes of this report.

Specifically, this volume summarizes the experimental studies of the various physical parameters of engine operation as a function of chemical variables. It also presents a summary of the literature pertaining to the chemistry of the individual propellants and propellant combinations used in the RCS engine. Finally, it describes the Bureau's experimental program in which both low pressure gaseous reactions and liquid phase reactions of the various propellant combinations were studied in a gas flow reactor and a simulated 2-D engine, respectively. Bureau results are compared to those of other investigators using similar experimental reaction vessels.

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BACKGROUND HISTORY

Many researchers have attempted to define and isolate the problems concerning the hard-start phenomenon (high pressure spiking during abnormal hypergolic ignition). Some of the factors proposed and evaluated by the researchers, such as ignition delay, impurities in the propellants, poor mixing, inappropriate oxidant/fuel ratio, and their direct and/or indirect effect on the chemical nature of the phenomenon are reviewed here.

Early in the history of rocketry, it has been noted that the hard start high pressure peaks observed at ignition in hypergolic engines could often be correlated to ignition delay times; that is, the longer the delay time the greater the possibility for the occurrence of a hard start. Ignition delay time is the time between the first appearance of propellants in the engine and ignition. There have been numerous attempts to correlate ignition delay with various parameters such as the molecular structural characteristics of the amine-type fuels, fuel/oxidant ratio, test container volume, and mixing rate. Schalla and Fletcher (1),³ note that attempts to identify ignition behavior of the amine and relate it to any single variable is a gross oversimplification of the problem. Numerous studies (2) of thermal ignition delays of gaseous mixtures of hydrocarbons and oxygen show that the logarithm of the ignition delay, when plotted against the reciprocal of the reaction temperature gives a straight line relationship, suggesting that the delay determining factor is related to the rate of the preignition chemistry. However, Kilpatrick and Baker (2) did not observe the same characteristics for hydrazine (N_2H_4) and nitric acid or for N_2H_4 and nitrogen tetroxide (NTO) systems. Spengler and Bauer (3) studied the effect of various factors on ignition delay in rocket engines using an unsymmetrical dimethylhydrazine (UDMH)/nitric acid system, and concluded that only for the specific engine examined could explicit relationships be established. The same conclusions have been reached by other investigators. We generally recognize two types of gaseous thermal ignition mechanisms: Those controlled by thermal transport and those controlled by the formation and propagation of free radical chains. Most researchers have attempted to fit the hypergolic systems into one of these two categories without complete success.

Shortening or lengthening the ignition delay time by various means can usually help to reveal the nature of the ignition phenomenon. In this vein, Weiss and coworkers (4) studied the effect of additives on ignition delay. Thirty-two additives were tested and all but one were added to the fuel; iodine was added to the NTO. Most of the additives were selected on the basis of their affinity for nitric oxide (NO), a substance present in the NTO and believed responsible for the hard start. The additives were found capable of changing the delay times, although not significantly. Shortened

³Underlined numbers in parentheses refer to items in the list of references preceding the appendix.

delay times were observed with Surfactant FC-126⁴ and Santomerse 85.⁴ The results of this study suggested that the miscibility of the two propellants may be one of the factors controlling the ignition delay.

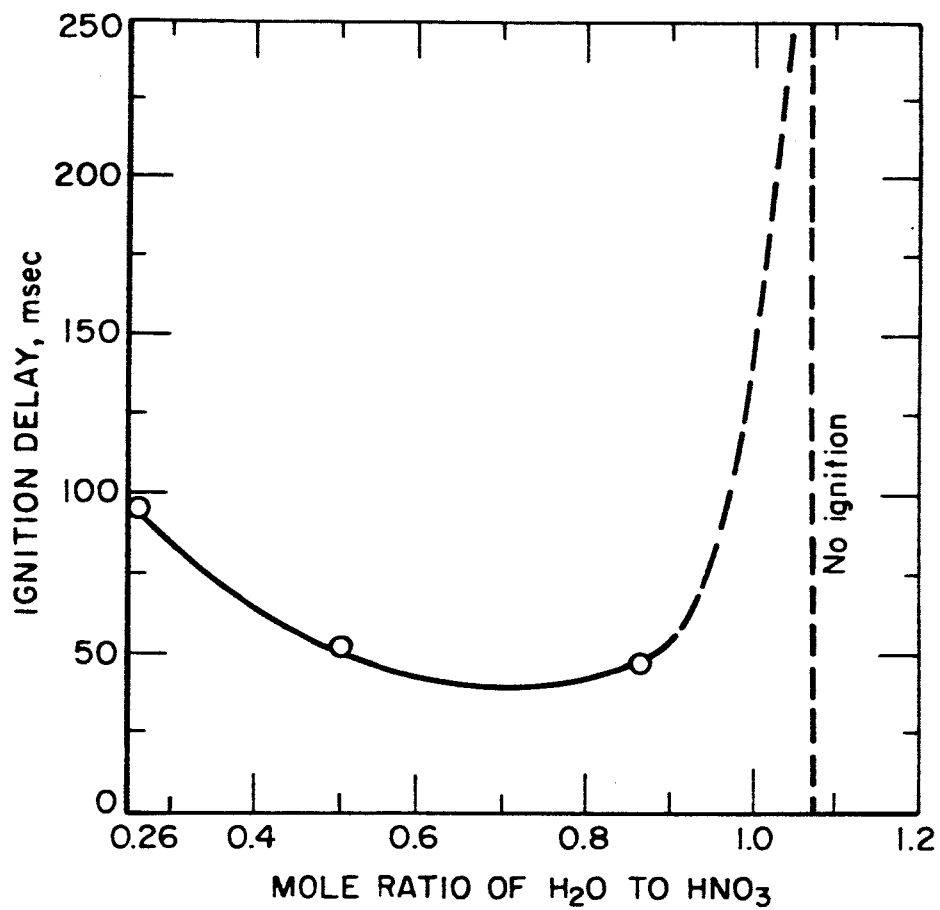
That the degree of mixing plays an important role in ignition delay is also shown when different types of injectors are used in an identical engine. For example, Kilpatrick and Baker (2) found shorter ignition delays for a jet impingement injection than for an open cup injector. Furthermore, Bernard (5), who measured the ignition delay in an open-cup injector and in a concurrent-jet injector, observed shorter delay times for the open cup. Bernard (5) suggests that the shorter delay times found in his open cup experiments are due to the lower momentum associated with the sprayed particles; in the concurrent-jet method where particle velocities are higher, ignition is delayed.

Griffin and Clark (6) measured the ignition lag time of impinging jet-type injectors. They found the degree of mixing was reduced as stream breakup occurred, increasing the lag time. Thus, it is generally agreed that mechanical as well as chemical causes affect ignition delay time.

One additive to oxidants that was often studied was nitrogen dioxide (NO_2). Ladanyi (7) added varying amounts of NO_2 to red fuming nitric acid (RFNA) which was then brought in contact with aniline, and with an aliphatic amine. With aniline, ignition delays were not dependent on NO_2 concentration; while with the aliphatic amine, there was a definite relation between ignition lag and percent NO_2 . Spengler and Bauer (3) found that in the UDMH/HNO_3 system the addition of NO_2 to the HNO_3 shortened the ignition delay. Gregory and Calcote (8) studied the burning of RFNA drops in N_2H_4 vapor. As shown in figure 1, water added to the RFNA, lowering the percent NO_2 in the acid, affects the ignition delay. With a water to nitric acid weight ratio above 1.1 no ignitions occurred; whereas for ratios below 1.1 ignitions were observed with a minimum in the ignition delay at a ratio of 0.7.

The effect of additives on ignition delay times was not the only factor studied. Seamans and Waser (9) examined the effect of nitric oxide (NO), acetonitrile (CH_3CN), and water on the ignition characteristics of monomethylhydrazine (MMH)/ N_2O and of Aerozine-50 (A-50)/ N_2O systems. They did not report ignition delays, but determined the minimum ignition pressures. In this study, the compounds were added to the fuel. NO is appropriate to study since it is usually added to the fuel to prevent stress corrosion in the titanium storage tanks. CH_3CN is added to prevent the growth of salt deposits in small passages in the N_2O lines. These additives were not found to have a pronounced effect on the ignition processes or on its activation energy.

⁴Reference to specific brands, equipment, or trade names in this report is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.



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FIGURE 1. - Ignition Delay of H₂O/HNO₃ Drops in N₂H₄ (96 pct) Vapor as a Function of H₂O/HNO₃ Solution Concentration.

Adelman (10-11) studied the system RFNA/aniline with additives consisting of strong oxidation catalysts such as ammonium metavanadate and ammonium dichromate and nitration catalysts such as iron salts. Adelman (11) considered three reactions to take place during the hypergolic reaction: Neutralization, nitration, and oxidation. He found that the iron salts were not effective in changing the delay time of the ignition, but that the metavanadate salt reduced the ignition lag. On the basis of these results, he concluded that the oxidation reaction controlled the ignition lag.

In another investigation of HNO_3 /fuel hypergolic reactions, in which the fuels tested were furfuryl alcohol and various solutions, Bernard (5) studied the effect of iron and vanadium salts as well as the effect of wetting agents and surfactants. He found that, in general, lowering the interfacial tension between the propellants decreased the ignition lag, apparently due to better mixing. Of the surfactants and wetting agents used, the nonionic agents of low molecular weights shortened the ignition delay, while organic compounds containing OH groups were especially effective when added to the nitric acid. The effect of the salts was not pronounced.

Another series of experiments in which additives were examined was reported by Skinner, Hedley and Snyder (12). In this study, the effect of additives on gas phase ignition of N_2H_4 /NTO was observed and the additives were added to the oxidant. They found that the additives had little effect on the concentration of NTO required for ignition. From this study, Skinner and coworkers (12) concluded that the ignition reaction proceeded through a thermal transport-controlled mechanism and not through a free radical mechanism.

In addition to additives, trace impurities in the propellants have been observed to affect the hypergolic reactions. Impurities in N_2H_4 for example include iron salts, sodium salt, water, ammonia, aniline, and toluene. In a study reported by Weiss and coworkers (4), slight differences in delay times, observed with each new batch of N_2H_4 , suggested that the presence of impurities in the N_2H_4 affected the ignition processes. Spengler and Bauer (3) similarly noted that stored propellants showed better ignition behavior than freshly distilled propellant. Muraca, Whittick and Crutchfield (13) studied long-term storage of N_2H_4 and proposed that N_2H_4 reacted with oxygen during storage to form $\text{H}_2\text{NNH-NH-NH}_2$ and water.

Baulknight (14) has suggested that alkaline metal salt impurities, present in N_2H_4 , could be responsible for the ignition delay and subsequent hard starts in the A-50/NTO propellant system.

The various factors that were studied by many researchers, only a few of which are cited here, show the complexity of the ignition mechanism and the many possible causes of ignition delay and consequently of hard starts, and exemplify the difficulty of finding an immediate remedy to the hard-start problem.

Correlations of the experimental results with theoretical studies have also been made. Crocco and associates (15-16) were among the first to propose a model of hypergolic ignition based on a combustion time lag parameter to explain observed combustion instability. It has been suggested that hard starts may be caused by such instabilities. Another theoretical study, concerned with nonlinear combustion instability and utilizing the concept of time lag, is that proposed by Burstein, Chinitz and Schechter (17). They defined the ignition delay as the time required for the principal oxidation reaction to occur. Their study indicated that the ignition delay was strongly dependent on the initial mixture temperature, but not on the initial pressure. In this respect, the study by Griffin and Clark (6) is of interest. They studied the effects of pressure and temperature on the ignition lag and found that lowering the temperature of the propellants resulted in decreased mixing, due mainly to an increase of the propellants' viscosity and, hence, undesirable. The effect of lowering the pressure below the propellants' respective vapor pressures increased breakup of the propellant jets. With the impinging jet-type injectors, they found that the degree of mixing was reduced when stream breakup occurred. When they measured the effect of both low temperature and low pressure, the effect on ignition was found to be synergistic.

Other ignition lag-related theoretical studies are cited in volume I of this report.

Although conflicting results indicate the necessity for more sophisticated studies, and although the test conditions in most of these ignition delay experiments do not always simulate the conditions found in the RCS engines at ignition, nonetheless, they served their purpose in indicating the salient features of hypergolic reactions.

CHEMISTRY OF INDIVIDUAL PROPELLANTS

Introduction

Not only are the hypergolic reactions between fuel and oxidant complex, but the individual propellants themselves are very reactive and capable of undergoing a multiplicity of reactions. Some of the more interesting and relevant of these reactions are briefly discussed here. They include the reactions of nitrogen oxides and N_2H_4 -type fuels. We believe that most of these reactions, such as the ignition, decomposition, and oxidation of these various propellants can take place, and probably do take place, in the RCS engine during actual flight conditions.

The reactions described here were studied by researchers utilizing laboratory-type equipment, not engines or simulated engine conditions. It has been suggested that in the engines, geometric parameters and materials of construction can influence the paths of reactions. Therefore, these effects should be taken into consideration before any conclusions regarding reactions in the engines can be drawn.

Reactions of Nitrogen Oxides

The oxidant N_2O_4 , or more precisely its monomer NO_2 , is a molecule with an odd electron, and its reactions belong to the classes typical of free radicals (18). NO_2 can undergo dimerization, addition to unsaturates, hydrogen abstraction, photolysis, decomposition, and reduction, in addition to sensitizing other chemical reactions.

It dissociates according to the reaction,

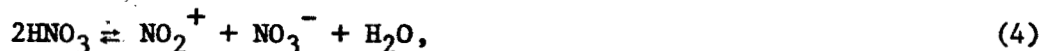


followed by the reaction



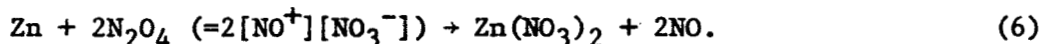
The degree of dissociation depends on both pressure and temperature. In view of these reactions, the presence of NO and N_2O_3 must also be considered in the engine reactions.

In dilute solutions of NO_2 in HNO_3 (19-21), the following reactions occur,



Infrared studies of these solutions fail to show the presence of NO_2 , at certain compositions, suggesting complete ionization.

Some support for the presence of the nitrate group in liquid N_2O_4 is also given (22) by the isotope exchange reaction,



Not only in solution does the nitrate ion form, it has been shown (23) to be formed in the photolysis of NO_2 and nitric acid vapor,



Other possible photolysis reactions include,



It appears that the presence of even trace amounts of water in either fuel or oxidant is undesirable. Unfortunately, water is formed as a by-product of many of the reactions that occur between the propellants, and it leads to the formation of nitric and nitrous acids according to the equation (24),



with low temperatures favoring the reaction to the right. Nitrous acid is unstable at room temperature and in solution readily decomposes according to the reaction,



However, this decomposition is comparatively slow in cold dilute solutions.

Low temperatures which are the rule for starting engines in space, due to propellant vaporization are, therefore, favorable to the formation of HNO_2 . It will be later shown that HNO_2 can, under suitable conditions, form the very sensitive explosive N_3H .

Another vapor phase reaction in which HNO_3 is formed is described by Wayne and Yost (25),



The rate of this reaction, which takes place with NO in excess, has been shown to depend strongly on the water vapor concentration. Reaction half times as short as 14 msec have been observed. When NO is not in excess, the following reaction predominates,



It is evident from all the above reactions that nitric acid, nitrous acid, nitric oxide, nitrogen trioxide and nitrate ions are probably all present in the engine in varying amounts, and as will be shown subsequently, all react with the N_2H_4 -type fuels.

In the presence of hydrogen, a thermal decomposition product of N_2H_4 , NO_2 reacts in the following manner (26),



providing another path for the formation of HNO_3 and HNO_2 .

The HNO radical has been reported by McLain (27), based on spectral studies, as an intermediate of the reaction between MMH and NTO. The spectrum of HNO was also observed following flash photolysis of nitric oxide and ammonia mixtures (28); the latter two have been suggested as intermediates of the A-50/NTO reaction. The HNO radical also reacts with NO. Holmes and Sundaram (29) have studied the inhibiting properties of NO and suggest that NO forms nitroso compounds when it combines with a free radical or an atom, according to the mechanism,



with the overall reaction,



The HNO radical can also be formed by the addition of NO to a hydrogen atom in the presence of a third body (30),



or eliminated by the reaction,



In addition to HNO, McLain (27) reports the presence of hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$), probably an HNO dimer, as an intermediate of the MMH/NTO reaction.

NO_2 reacts with stainless steel (31) to form two compounds; one a solid having the composition $\text{NO} \cdot \text{Fe} \cdot (\text{NO}_3)_4$, and the other a liquid with a complex, unknown structure. Both materials are soluble in NTO. When NTO is cooled, the solid compound and the crystallized liquid precipitate in the injector lines and obstruct the flow of NTO.

NO_2 also reacts with formaldehyde (32-33) at a rate that is strongly pressure and temperature dependent. Formaldehydes and their reaction products, such as formaldehyde dimethylhydrazone (34), have been found in the reaction products of the studies conducted by the Bureau in the low pressure (>1 torr) gas flow reactor using substituted N_2H_4 fuels, described later in this volume. NO_2 and formaldehyde react according to the equations,



At 180° C and depending on the pressure, the reaction becomes explosive. At low temperatures, formaldehyde is oxidized by NO₂ (35), with the rate determining step being,



this also being another path for the formation of nitrous acid.

Lawver and Hersh (36) report finding that weak shock waves passing through cavitated (boiling) NTO, generated pressure spikes greater than 200 atm. They suggest that the spike is a consequence of the very fast (half life 1 μsec) reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ behind the shock. The authors further suggest that similar pressure spikes might be observed during RCS engine ignitions.

Reactions of Hydrazine Fuels

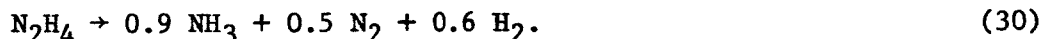
The decomposition, oxidation, and combustion of N₂H₄ has been studied by many investigators. A summary of only a small part of the relevant literature is presented.

Since many have suggested that the propellant impurities may be significant factors in the hard-start phenomenon, we list here the major fuel impurities: N₂H₄-H₂O, ammonia, aniline, toluene (100-300 ppm), iron (1 ppm) and sodium salts; MMH-N₂H₄, UDMH, H₂O, ammonia and methylamine; USMH-ammonia, H₂O, dimethylamine, methylene, dimethylhydrazine, and sodium salts. Some researchers believe that these impurities catalyze the decomposition of the fuels, particularly during storage, forming among other things nitrogen, hydrogen, and ammonia. These gases dissolve in the fuels and are later released when injected into the engine. The impurities are also believed to trigger side reactions in the engine. Sodium salt such as the hydride or amide, for instance, reacts with N₂H₄ to form sodium hydrazine, as follows,



Sodium hydrazide itself explodes violently on reaction with oxygen or on heating above 100° C. It also undergoes a multitude of reactions with organic compounds, especially when in a N₂H₄ solution. Baulknight (14) has pointed to the possible adverse effects of sodium salts on the hypergolic system, and particularly when the fuel is UDMH, which is likely to contain larger amounts of the impurity. These salts also are believed to contribute to the formation of AN.

The decomposition of N₂H₄ and N₂H₄-type fuels has been studied by Eberstein and Glassman (37) who measured the rate of decomposition of gaseous N₂H₄. They suggest the following reaction occurs,



They found that the decomposition was strongly inhibited by water. They also found that toluene suppressed decomposition and helium, in excess, completely stopped it. Axworthy and coworkers (38) conducted extensive measurements of the decomposition of N_2H_4 in contact with various metal and nonmetal surfaces. They found that the decomposition of N_2H_4 was strongly acid-catalyzed; this was most clearly evident in the presence of metal surfaces--decomposition proceeded 200 times faster in 316 stainless steel than in pyrex containers. The rate in 347 stainless steel vessels was four times faster than it was in the glass vessels. In another study (13) of decomposition during long-term storage of N_2H_4 , the decomposition proceeded according to the reaction.



with a much smaller decomposition via,



and with traces of air dissolved in N_2H_4 , possibly even,



thus, indicating that the decomposition favored the formation of ammonia and nitrogen with smaller amounts of hydrogen and water.

Shock tube studies of the decomposition kinetics of carefully purified and dried N_2H_4 vapors diluted with argon were made by McHale and coworkers (39). They devised the following expression for the decomposition rate, $K = 10^{13} e^{-54 \text{ kcal}/RT} \text{ sec}^{-1}$, and found in the temperature range 970° to $1,550^\circ$ K, the kinetics to obey a simple nonchain mechanism,



The addition of small traces of H_2O or CO_2 to the purified N_2H_4 did not affect its decomposition rate. A review of other research studies dealing with decomposition of N_2H_4 is presented by McHale (39).

Papazian (40) studied the decomposition of solid N_2H_4 when irradiated with charged particles, and found the decomposition process to be complicated and to proceed in several steps. Based on the ratio of nitrogen and hydrogen gases evolved, Papazian suggests that triazene is an intermediate of the reaction, which then decomposes to nitrogen and ammonia,



This mechanism provided an explanation for the high ratio of nitrogen to hydrogen observed by Papazian (40).

Studies of burning velocities also help in understanding mechanisms of N_2H_4 decomposition and oxidation. The burning velocity of the N_2H_4 decomposition flame and parameters affecting it were measured by many researchers. Breen and Lawver (41) burned liquid N_2H_4 containing 10 pct H_2O and found the burning velocity to be 19 pct slower than the burning rate of anhydrous N_2H_4 . A similar trend was observed by Eberstein and Glassman (37). Similar studies by Peter Gray and coworkers (42), using gaseous N_2H_4 and diluents such as helium, argon, nitrogen, hydrogen, and ammonia showed that nitrogen and hydrogen, with higher heat capacities than argon and helium were more effective in reducing the burning velocity. Lawver and Breen (43) also studied the effect of additives on the burning velocity of drops of N_2H_4 . The following additives were chosen to study the effect of specific chemical groups on the combustion:

Urea	NH_2 radical source
Dimethylsulfoxide ...	CH_3 radical source
Fluorobenzene	H atom scavenger
Phenylhydrazine	NH , NH_2 radical source
MMH	CH_3 radical source
Pyridine	-

Each of these materials affected the burning velocity differently. Urea and phenylhydrazine increased droplet burning, while MMH and pyridine reduced the velocity. Nitromethane and urea caused droplet ejection from the burning fluid, while dimethylsulfoxide caused droplet shattering and fluorobenzene brought about droplet sputtering. No general conclusions as to the effect of the specific chemical species could be drawn; the only effect discernible was that associated with changing the boiling point of N_2H_4 .

In many of the investigations concerned with the decomposition of gaseous N_2H_4 , the presence of NH , NH_2 , and N_2H_3 radicals was observed by spectral techniques. Consequently, many of the mechanisms describing the kinetics of combustion utilize these radicals as intermediates of reactions, as for example,



The decomposition of N_2H_4 and of UDMH vapors is strongly dependent on the vessel conditions as shown by Gray and Spencer (44). Surface area, surface to volume ratio, wall material and inert gases are all contributing factors and should be considered when comparing and evaluating results.

N_2H_4 and its homologs are very reactive. N_2H_4 reacts with oxidizing gases such as O_2 , NO , and NO_2 . Since these gases are present in the RCS engines as decomposition products, impurities, or as intermediates, the reactions of N_2H_4 with these gases are of significance.

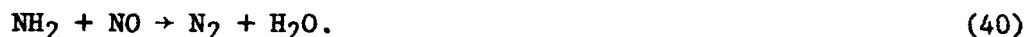
Gray and Spencer (45) studied the reactions between N_2H_4 and NO , as well as the reactions of H_2 and NH_3 , decomposition products of N_2H_4 , with NO .

While N_2H_4 reacted hypergolically with NO , neither H_2 or NH_3 ignited nor appeared to react. In general, NO is not as reactive an oxidant as O_2 , but the presence of NH and HN_2 radicals often changes this order. This was demonstrated by Hall (46). He found that the $\text{N}_2\text{H}_4/\text{NO}$ flame showed the NH and NH_2 spectral bands to be weaker than those observed in the $\text{N}_2\text{H}_4/\text{O}_2$ flame, thus suggesting the scavenging of NH and NH_2 by the NO .

The combustion of N_2H_4 with NO can be either deflagrative or detonative, depending on the $\text{N}_2\text{H}_4/\text{NO}$ concentration. A stoichiometry favoring is the following,



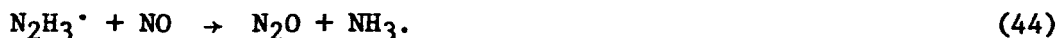
The mechanism for the stoichiometric reaction is discussed by Bamford (47), who suggests the following,



NO is readily excited by certain wavelengths of light (48) and the resultant excited molecules can enter into even more energetic reactions with N_2H_4 . Bamford (49) irradiated NH_3 and N_2H_4 in the presence of NO and found that the primary photolytic reaction produced NH_2 and N_2H_3 radicals, respectively, and suggested the mechanism,



and



Serewicz and Noyes (50) repeated the experiment with NH_3 and believe that NH_2 formed an adduct with NO , which then disappeared forming N_2 and H_2O . They did not identify the adduct. N_2H_4 may react in similar fashion, forming an adduct. The role of light and radiation, in general, on the hypergolic reactions has not been studied, although most of the molecules present at various times in the engine are radiation sensitive and there exists a broad spectrum of radiation in the engine during ignition and subsequent combustion.

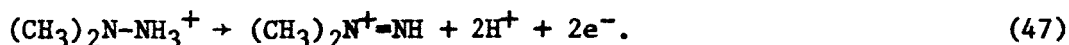
Winning (51) studied the reaction of gaseous N_2H_4 with O_2 and found it to be predominantly a surface phenomena, independent of the diluent N_2 concentration, and following the reaction,



In another series of experiments, Bowen and Birley (52) studied the reaction of gaseous N_2H_4 and O_2 and found peroxides formed on the reaction vessel's glass walls. Surprisingly, in these experiments the presence of inert gases increased the rate of the reaction. It was proposed that the oxidation was not a branching or long-chain reaction but rather occurred in steps. In another study in a zirconia flow reactor, the slow reaction of NH_3 and air was found to be influenced by the aging zirconia; the fast reaction or NH_3 combustion was not affected (53). It was further noted (53) that the reaction could easily shift from a fast to a slow reaction, by momentarily stopping the fuel flow or changing the O/F ratio.

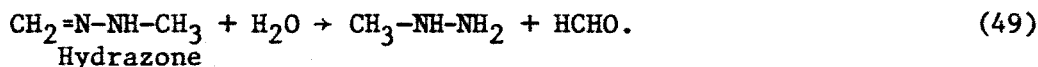
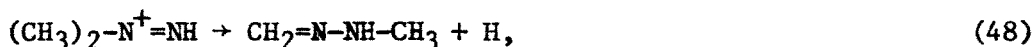
The substituted hydrazines, MMH and UDMH, in many ways similar to N_2H_4 , are more organic in nature and have many properties similar to those of amines in forming salts. Methodical observations of the reactions of UDMH and dimethylhydrazine with oxygen were carried out by Gray and coworkers (44). They found that the reaction paths depended on the experimental conditions (for example O/F ratio, vessel volume to surface ratio, diluent concentration) and ranged from chemiluminescent oxidation, weak ignitions, and multiple ignitions up to violent explosions.

Another approach to the study of oxidation of substituted hydrazines was taken by King and Bard (54), who used the method of electrooxidation and obtained interesting results. They present the following mechanism for a few of the steps in the complicated reaction of UDMH oxidation,

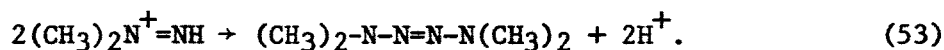
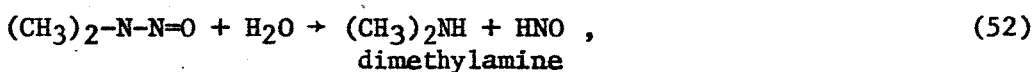
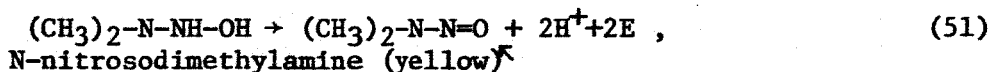
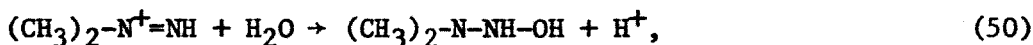


forming a substituted diazene ion. The products of oxidation by electrolysis included nitrogen, methanol, formaldehyde, dimethylamine, and an unidentified yellow, soluble product. Diazene has been shown, by McBride and Kruse (55), to form tetrazene in neutral or alkaline solutions; while in acidic solutions, the dimethyldiazene undergoes slow decomposition.

These results are of particular interest to this study because products obtained by the Bureau in the gas flow reactor experiments using UDMH, described in a subsequent section, included tetrazene and formaldehyde. The formation of formaldehyde (and similarly of methane) can be explained (56-57) by the mechanism,

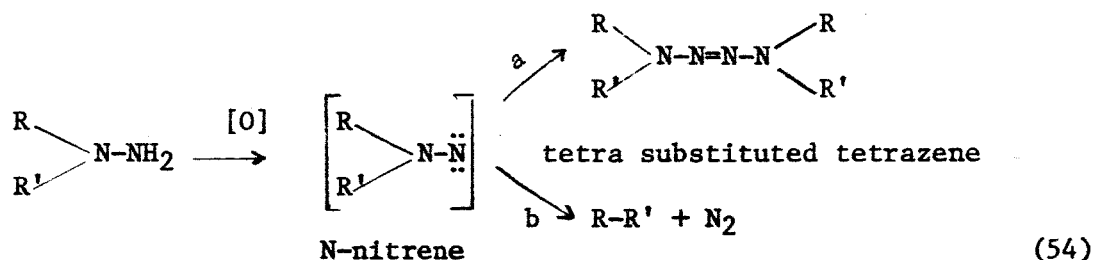


Other possible steps are,



It is not surprising that the oxidation products of UDMH are so varied; the decomposition products also were found to be numerous and included methane, ethane, propane, ammonia, and dimethylamine (58).

The products of the decomposition and oxidation of UDMH are dependent on reaction conditions. To show the multiplicity of possible products, we will cite just a few more examples. When a saturated nitrogen-nitrogen bond (59) is oxidized, the product is often nitrogen or some intermediate compound which can be made to evolve nitrogen. A primary amine function permits several reactions. Two possible products, proceeding through an N-nitrene intermediate which is formed via the abstraction of hydrogen, are:



Products of oxidation are determined by the nature of the substituents (R and R'); however, the majority of such oxidations yield the tetrazene (path a). Path b, termed the "abnormal" oxidation, requires that the substituent groups be capable of stabilizing the intermediate fragments as a new carbon-carbon bond is formed. The "abnormal" oxidation proceeds readily in heterogeneous oxidizing systems (e.g. ethanol-mercuric oxide), with a larger surface area of the oxidizing agent increasing the rate of nitrogen evolution. In more homogeneous media, the tetrazene formation is often favored (e.g. mercuric acetate in ethanol solution). When the

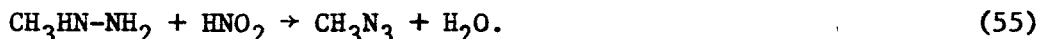
substituted groups are methyl, ethyl, or similar alkyl groups, they are unable to stabilize the intermediate carbon fragments (it is yet unknown whether they are ionic or free radicals) and thus they discourage the cleavage of the carbon-nitrogen bond or path b.

Oxidizing agents such as ethylazodicarboxylate, mercuric oxide, ferric chloride, and hypochlorous acid also give tetrazenes (57).

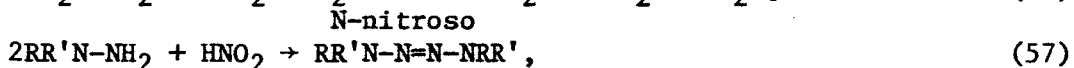
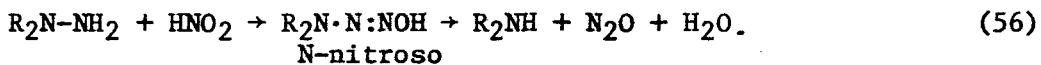
McBride (55) has shown that the formation of tetramethyltetrazene depends on the pH of the solution. When UDMH was oxidized at low temperature with potassium bromate in HCl, the tetrazene was not formed; while if the acidic solution was carefully neutralized at low temperatures, the tetrazene was formed in nearly quantitative amounts.

Tetrazenes are pale yellow oils or low melting solids (57). All pyrolyze above 100° C, liberating nitrogen and forming tetrasubstituted tetrazenes. Renouf (60) found the decomposition products of the tetramethyltetrazenes to include dimethylamine, methylamine, nitrogen, and formaldehyde. Similar products of decomposition of the tetrazene are cited by Gowenlock and his coworkers (61).

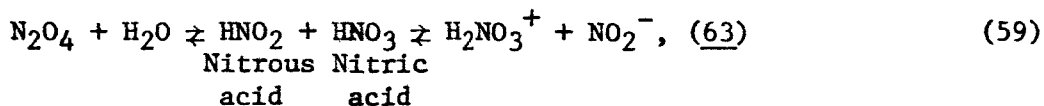
The possible oxidizing agents of UDMH in the engine are NTO or HNO_2 as well as other nitrogen oxides, all of which can be formed in the engine from NTO and water. These oxidizers react with N_2H_4 and MMH. Of special interest as an oxidizer is HNO_2 , which reacts differently with the different fuels. When HNO_2 reacts with N_2H_4 , it is known to form N_3H ; this reaction is discussed in detail in the section describing reactions of propellant combinations, later in this volume. With the mono-substituted N_2H_4 , MMH, HNO_2 forms a methyl azide, according to the reaction,



While oxidation of UDMH by HNO_2 proceeds, according to Sidgwick (62) as,

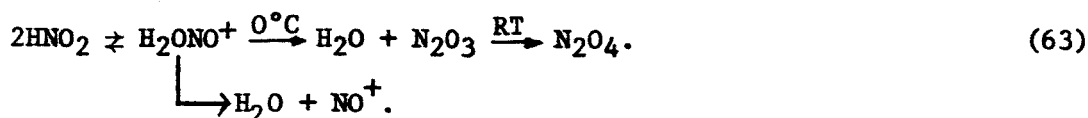
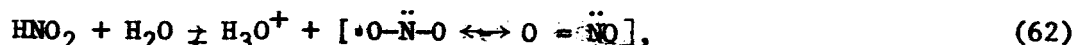


The previous few reactions are the simplest possible that could occur, assuming the presence of HNO_2 only, but in fact NTO and H_2O , both present in the engine, can form independently or together a multiplicity of oxidizing compounds as shown here:





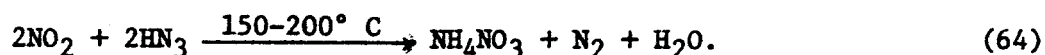
Other possible steps (64)



These are only a few of the probable reactions, but they clearly indicate the complexity of the chemistry of the hypergolic propellants in the engine.

NTO, through its reaction products with H_2O , induces simultaneously nitration as well as oxidation. The nitration route depends on the relative amounts of HNO_3 . When HNO_3 is predominant and the concentration of HNO_2 and other oxides of nitrogen is small, nitration through nitrosation is of no importance; while when HNO_2 is present in large amounts, nitration through nitrosation is dominant, with the attacking species being NTO and NO^+ , not N_2O_3 . The presence of small amounts of nitroso compounds and nitrosamines, detected in the gaseous products of a few UDMH/NTO flow reactor experiments, evidences once more the formation of HNO_2 and its presence in the hypergolic reactions.

That ammonia (NH_3) is present, albeit in small quantities, in the various N_2H_4 fuels as an impurity has been mentioned earlier. It is also one of the decomposition products of these fuels. NH_3 reacts with NTO (even solid NTO) (18) and yields water, nitric oxide, nitrogen, ammonium nitrate, nitrous oxide, and ammonium nitrite. In the gas phase, the reaction proceeds according to,



The reaction is third order and strongly temperature dependent.

PROPELLANT REACTIONS AND RELATED PHENOMENA IN THE TWO-DIMENSIONAL (2-D) ENGINE

Introduction

This section describes the Bureau's approach to the chemical aspect of the hard-start phenomenon. Our investigation concentrated primarily on the RCS engine preignition period; that is, the time interval between the first

appearance of propellant in the combustion chamber and subsequent ignition. With nonhypergolic propellants, this involves the physical activities of injection, vaporization, and heterogeneous dynamics of the propellants; with hypergolic propellants chemical reactions also occur.

A 2-D plastic engine having the same L^* ⁵ (27.3cm) as the Apollo RCS engines was used for this investigation. The 2-D experimental engine was operated with the same propellant flows and environmental conditions as the RCS engines. The propellant systems investigated included NTO as oxidant and N_2H_4 , MMH, UDMH, and A-50 as fuels.

Because the quantity of reaction products deposited in the 2-D engine study was insufficient for a detailed chemical analysis, a gas flow reactor, which could generate larger amounts of the residue under controlled conditions and provide for time resolution of the reaction spectrum, also was used. The flow reactor also afforded, among other things, easier control of the O/F ratio and simpler means for introduction of inert gases and for sampling the gaseous reaction products. Both experimental programs are discussed in the following sections.

Experimental Apparatus

Figure 2 shows the essential details of the 2-D plastic engine used in these studies. To avoid the post-shutdown propellant dribble that normally follows the closure of the propellant valves in the RCS engines, a piston displacement technique was selected for injecting the propellants. The volume of propellants used in these experiments was usually just sufficient to avoid an ignition, since a larger volume usually led to ignition and we wanted to avoid contaminating the preignition products with combustion products. The pistons were made of Teflon and separated the liquid propellants from the hydraulic driving fluid, which was usually water. An aluminum foil diaphragm and a Teflon O-ring sealed the bottom of the propellant reservoirs which had glass liners to protect the plastic surface from attack by the corrosive propellants. A hydraulic line connected the high pressure driver gas (N_2) to the pistons to increase the system response and avoid gross waterhammer effects. To insure reliable, simultaneous rupture of the two aluminum foil diaphragms, it was necessary to use nitrogen pressure in excess of 20 atm. When lower pressures were used, the aluminum diaphragms did not always rupture simultaneously. This resulted in a "lead/lag" effect; that is, the injection of one propellant prior to the other, and was utilized a few times just for this purpose. By varying the nitrogen pressure from 20 to 41 atm, propellant flow rates ranging from about 90 to 140 grams/sec were obtained. Further adjustments in the flow rates could be obtained by changing the diameter and length of the injector capillaries. A piezoelectric pressure transducer, flush mounted in the engine wall, monitored the preignition pressurization process and a high-speed (16,000 frames/sec) camera observed events occurring within the combustion chamber.

⁵A design parameter of the RCS engine equal to the ratio of the internal volume of the combustion chamber of the engine to the throat area.

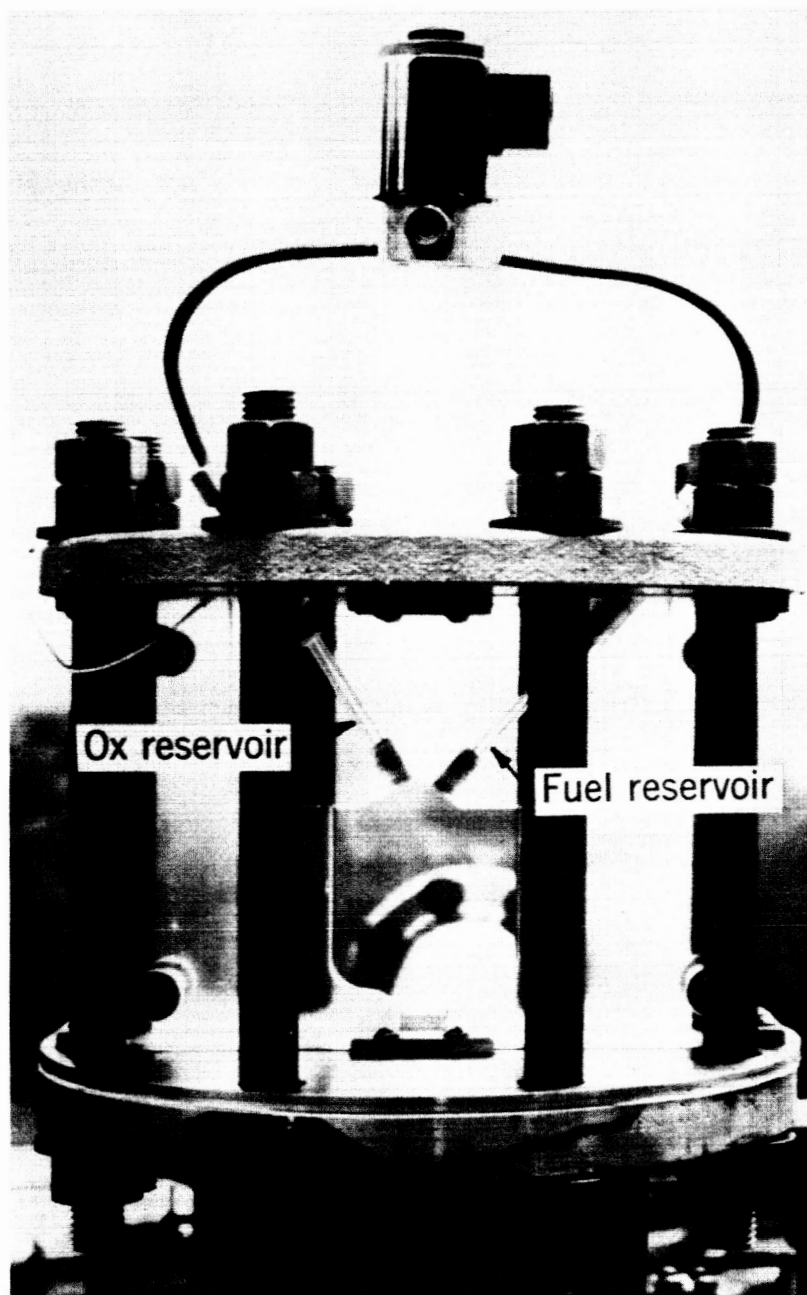


FIGURE 2. - Two-dimensional (2-D) Plastic Engine.

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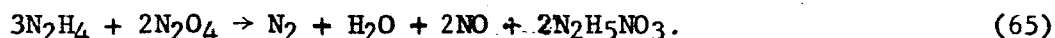
Information regarding the postcombustion period of engine operation also was sought. In order to simulate postcombustion conditions in the 2-D engines, the propellants were injected into the engine under their vapor pressure. To accomplish this, tiny electrically initiated explosive-actuated pistons, positioned under the aluminum diaphragms, punctured the diaphragms without exerting any pressure on the Teflon plugs.

In addition to analyzing the reaction products, it also was important to identify the reaction sites in the engine and determine the physical phase of the reactants during reaction. The following types of reaction alternatives appeared possible: (1) A fuel deposition on the engine walls and subsequent reaction with the NTO vapor; (2) a reaction in the liquid streams from which the resultant condensed-phase products migrate to the walls; and (3) a homogeneous vapor-phase reaction. To better distinguish between these alternatives, a special sampling surface was built into the 2-D engine. This unit was mounted flush with the engine wall to avoid altering the engine geometry. It consisted of a liquid nitrogen cooled surface, thermally isolated from the rest of the engine. The low temperatures prevented any reaction between materials that deposited on the sampling surface during a run. An exploded view of this sampling device is shown in figure 3, while an assembled engine module, with the sampling device in place, is shown in figure 4.

The engine gaseous reaction products exhausted out the combustion chamber throat into a 67-liter cylindrical plenum tank, and the complete assembly was evacuated prior to and during tests. When desired, the plenum tank could be cooled with LN₂ to a temperature of at least -100° C. In this way, the condensable combustion products in the plenum tank could not return to the engine combustion chamber. McLain (65), who used an identical engine but an uncooled plenum for studying the same propellant combinations, actually observed a reversal of propellant flow during preignition. Figure 5 shows a view of the experimental assembly.

Experimental Procedure

To conduct a run, the facility was evacuated to a pressure of 1 to 10 μHg. The injected propellants usually flowed for approximately 5 msec; ignition, if it occurred, took place at the end of this time. When ignition did occur, the resulting pressure most often destroyed the plastic engine. In most tests the volume of the fuel was 0.25 ml; the volume of the oxidant varied according to the stoichiometry of the respective fuel. The basis for stoichiometric calculations was complete conversion of the fuels to the respective nitrates, as for example in the case of N₂H₄ according to reaction,



Increasing the volume of the fuels to 0.5 ml, and increasing the volume of the oxidants respectively, consistently resulted in explosive destruction of the engines.

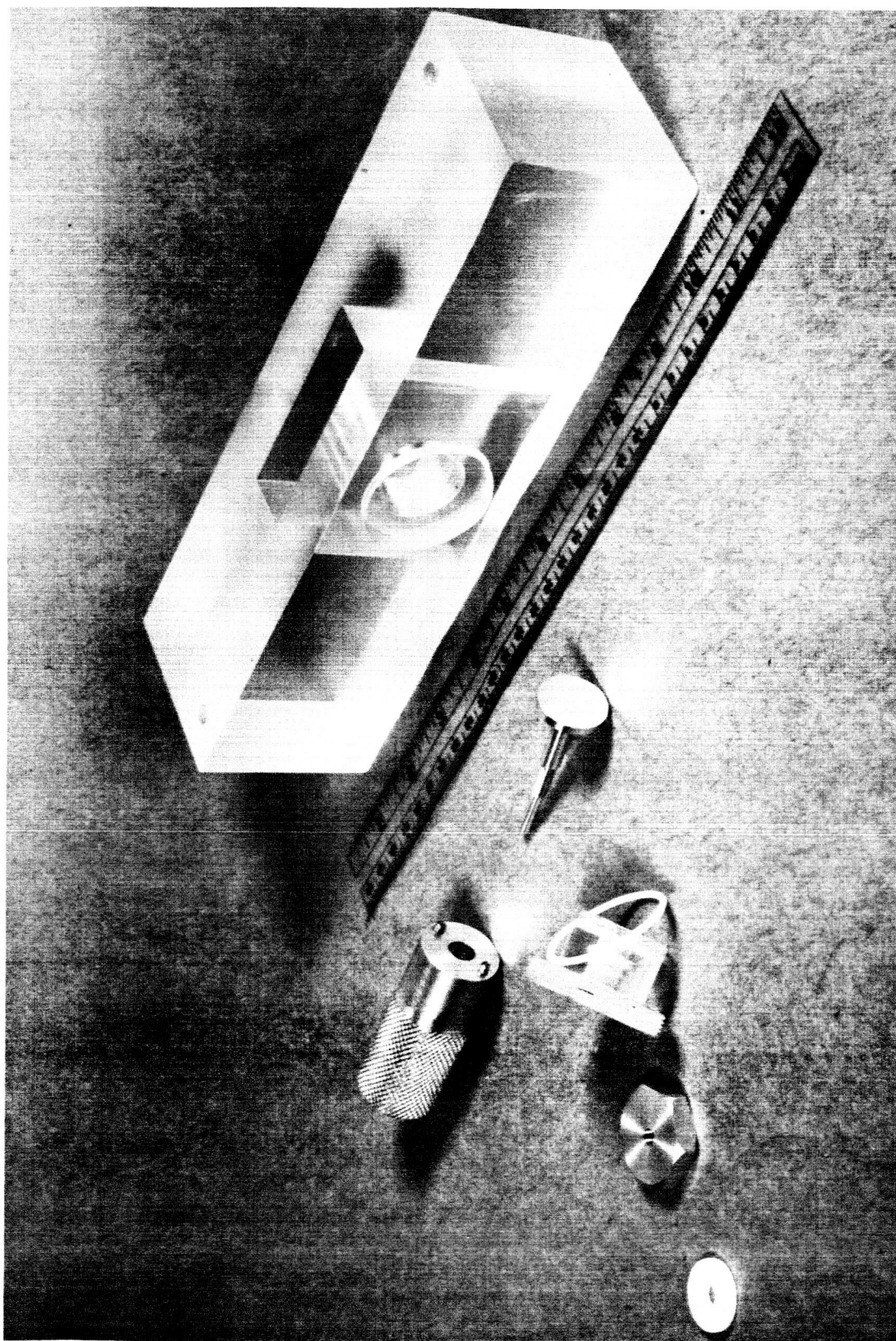


FIGURE 3. - Low Temperature Sampling Device; Exploded View.

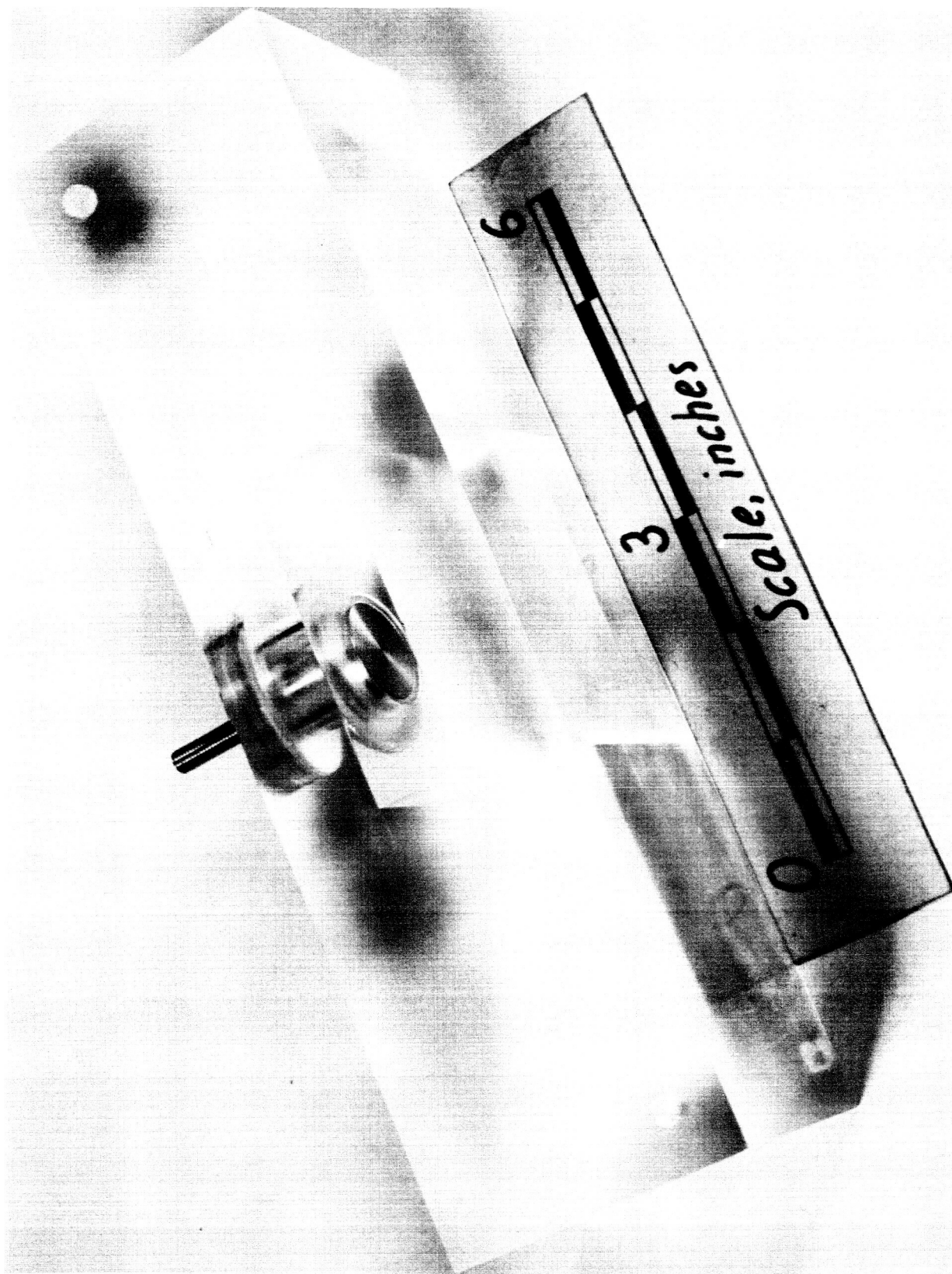


FIGURE 4. - Low Temperature Sampling Device: Assembled in 2-D Engine Module.

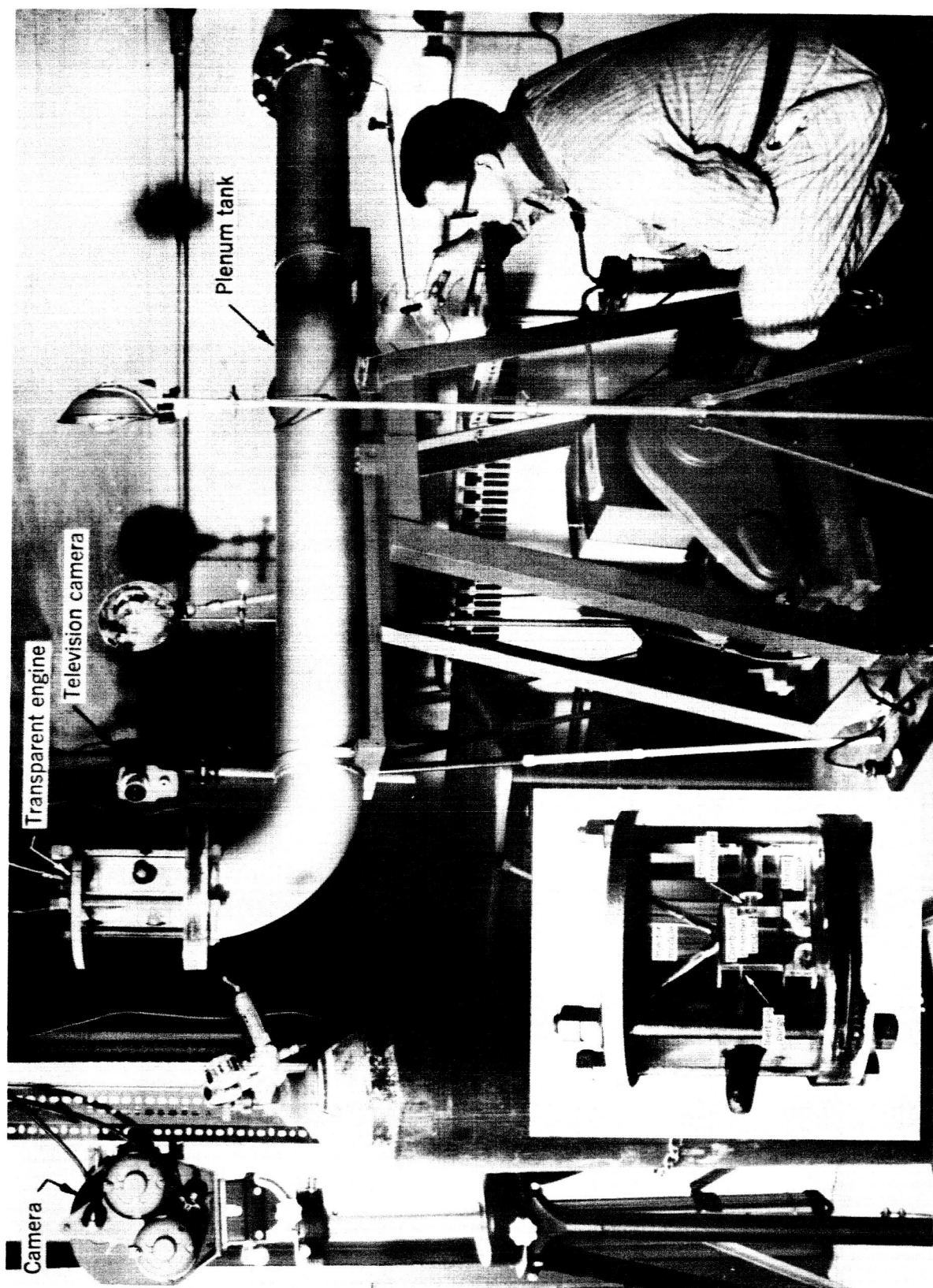


FIGURE 5. - Complete 2-D Engine Test Assembly

The engine was disassembled after every run, cleaned, reassembled, and its injection section refilled with propellants in preparation for the next run. Smaller and larger scale engines (1-lb thrust, 22-lb thrust, and others) that were tested by other researchers, were fired in a continuous pulsed mode, and consequently, accumulated large quantities of residues on their walls. The quantity of reaction products accumulated in the various engines depended also on the attitude of the specific engine during the test.

Following each run, a 0.1 mg sample of the reaction product was removed from the engine walls for analysis by infrared spectroscopy, usually using a potassium bromide matrix. The resultant spectra were identified by comparison with the spectra of the pure, standard materials shown in volume III.

Since nitrates predominated in the residues, an additional, quantitative test for total nitrate formed also was made via precipitation of the nitron nitrate. Nitrites, dinitrates, and azides also react with nitron to form nitron nitrates. The nitrites and azides are not very stable; even when they do form in the engine, their lifetime is usually short at room temperature and at ambient pressure. Although some of the infrared spectra of the residues showed the presence of the nitrite ion, it is believed to be evidence for the presence of unreacted oxidant or possibly ammonium nitrite. Dinitrates were very seldom detected in the infrared spectra of the residues. Based on these premises, it was assumed that the residues consisted mainly of the fuel nitrates, and the calculated nitrate concentrations were based on this assumption.

The purity of the propellants used in these studies was as follows: N_2H_4 , 97.5 pct; MMH, 98.0 pct; A-50, 98.2 pct; UDMH, 99.7 pct; and NTO, 99.0 pct. All materials were used as received, without further drying or purification.

The parameters studied in the 2-D engine included the propellant injection rate, the fuel type, and the O/F ratio. The reaction products (residues) were identified in as great detail as possible and the quantities of nitrates in these products for each run were determined.

Residues obtained from MSC and from the Marquardt Corp., during their engine-qualifying tests, were analyzed at the Bureau prior to the initiation of this study. The results of these analyses provided guidelines for our analytical procedures. It is important to remember, however, that in tests by other investigators in which the engine was fired repeatedly for a very short time period (with a firing cycle of 10 msec on and 20 msec off) the temperature of the engine walls was higher than in the Bureau's single firing. Since some of the residues were found to be heat sensitive, and either dissociated or decomposed at higher temperatures, the quantity and chemical composition of the residues depended on the engines tested and on testing conditions.

The residue samples sent by MSC and the Marquardt Corp., were separated by freeze drying and the resultant fractions analyzed. The liquid portions were analyzed by gas or liquid chromatography, and the solid portions by infrared spectroscopy. H_2O and HN were the major constituents. This was the first positive indication that HN was an important, and perhaps, major constituent in the residues, especially in the residue from the tests with N_2H_4 . Unfortunately, many of these samples may have undergone both physical and chemical changes by the time they reached the Bureau. But the consistent presence of HN coupled with the known fact that HN does not decompose below $300^\circ C$, suggested strongly that HN formed as an original reaction product rather than as a later decomposition product. Since HN was the major product in the residue of N_2H_4 , we presumed that the other fuels also would form nitrates in their reaction with NTO. And, since the chemistry of these materials suggested the possible formation of dinitrates, nitrites, azides, and tetrazenes, all of which might accumulate in the residues, we prepared pure samples of the nitrates of all the fuels as well as pure hydrazine dinitrate, hydrazine nitrite, hydrazine azide, and tetramethyltetrazene as standards in subsequent identification of residues. Dilute and concentrated solutions of the purified nitrate salts in their respective fuels also were prepared. The infrared spectra of all these standards, and the x-ray spectra of many of them also were obtained.

Results and Discussion

Although we concentrated on the chemical aspects of the reactions in the engine, and minimized or eliminated any change in physical variables, it is to be remembered that such physical aspects as mode of injection, degree of mixing, and local O/F ratio--to name just a few--are not always easily controlled. With this in mind, it is understandable that even though most of our runs were conducted with stoichiometric mixtures, we did detect in many of the residues both unreacted fuel and oxidant. The unreacted propellants, at times, interfered with the identification of the reaction products, and in the case of excess unreacted oxidant, led to undesired reactions with KBr, forming potassium nitrate.

The infrared spectra of the residues collected in the 2-D engine runs did show that nitrates predominated, although not always were these nitrates the respective fuel nitrates as initially surmised.

When the test fuels were N_2H_4 or MMH, they formed their respective nitrates, HN and monomethylhydrazine nitrate (MN). It was, therefore, expected that UDMH will react with NTO to form unsymmetrical dimethylhydrazine nitrate (UN); likewise, A-50 would form a mixture of HN and UN. However, analysis showed that ammonium nitrate (AN) was the major product in the residues of the UDMH tests, while in the tests with A-50, neither AN nor UN were found in its residue in any large quantity, but mostly HN or HN in unreacted fuel or in acidic solution. A careful examination of the infrared spectra of residues of A-50 tests showed the presence of very small amounts of AN and/or UN. Similarly, a close inspection of the infrared spectra of residues of UDMH tests did reveal the presence of peaks of nitrates other than AN, in small quantities, and possibly they are the

peaks of UN (fig. 6). Figures 7 and 8 show infrared spectra of residues of A-50 experiments which were prepared in a KBr matrix, and in the original liquid phase with no matrix, respectively. This was done because there was some concern that pressing the residue with KBr may change its composition.

Representative infrared spectra of liquid residues of N_2H_4 /NTO and MMH/NTO experiments are shown in figures 9 and 10.

As was explained earlier, unreacted propellants were anticipated in the residues; sometimes, though, a decision regarding the causative of every peak in the spectra was not simple. As an example, in figure 7, in addition to the HN peaks a relatively strong peak, usually associated with the NO_2 ion, is seen at approximately 7.8 to 7.9 microns. This peak could indicate the presence of either a nitrite or unreacted oxidant; indeed, this test was made under oxidant-rich conditions so that the presence of unreacted oxidant is not unexpected. But this fact in itself is not enough evidence for disclaiming the presence of a nitrite. The preparation of small quantities of the UN standard under carefully controlled conditions was difficult, and attempts to prepare larger amounts of UN were far from successful. During the evaporation step, when gentle heating was required, slight color changes were often noted in the evaporating solutions; when this occurred, the end product was usually AN. These latter findings offered an explanation of the UDMH 2-D engine tests. UN is very sensitive to heat; the temperatures generated in the 2-D engine during tests may be enough to convert UN to the AN in the UDMH residues.

The results of the A-50 tests also can be explained. N_2H_4 is considerably more reactive than UDMH and since, in most cases, the UDMH experiments were conducted with oxidant-lean mixtures, the presence of HN as the main ingredient in the residues of A-50 runs is quite understandable. N_2H_4 , the more reactive, reacted with the small amounts of the oxidant and not much oxidant remained for reaction with the UDMH portion of the A-50.

When the infrared spectrum of AN is compared with those of the various fuel nitrates, one fact clearly stands out. There is only one major peak in the AN spectrum compared to the multiple peaks of the other nitrates; this peak is shared by all nitrates; the other peaks are specific to each compound and assist in the identification of each. In order to assess the effect on the infrared spectra of the presence of small or large amounts of AN in another fuel nitrate, infrared spectra of various mixtures of HN and AN were obtained. These studies demonstrated that the presence of AN in another nitrate is not masked by the other nitrate. Evidence for the presence of AN is clearly seen in the spectrum of the mixture. The relative heights of the absorption peaks in the original fuel nitrate, in this case HN, are a function of the concentration of AN in the mixture. Attempts to obtain a quantitative measure of the percent of AN in the prepared HN-AN mixtures were only moderately successful, but the insight gained from this study was beneficial in the identification of small quantities of one nitrate in a mixture whose major constituent was another nitrate.

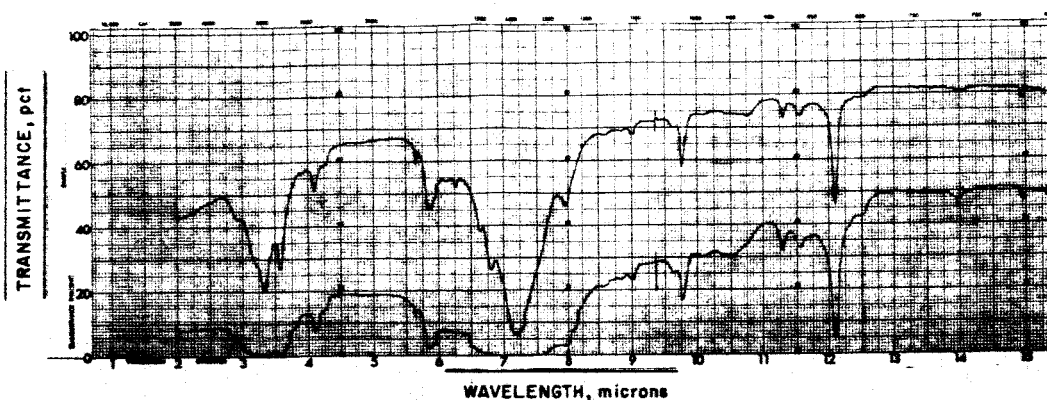


FIGURE 6. - Infrared Spectrum of Reaction Product in 2-D Engine Test; μ DMH/NTO (KBr Matrix).

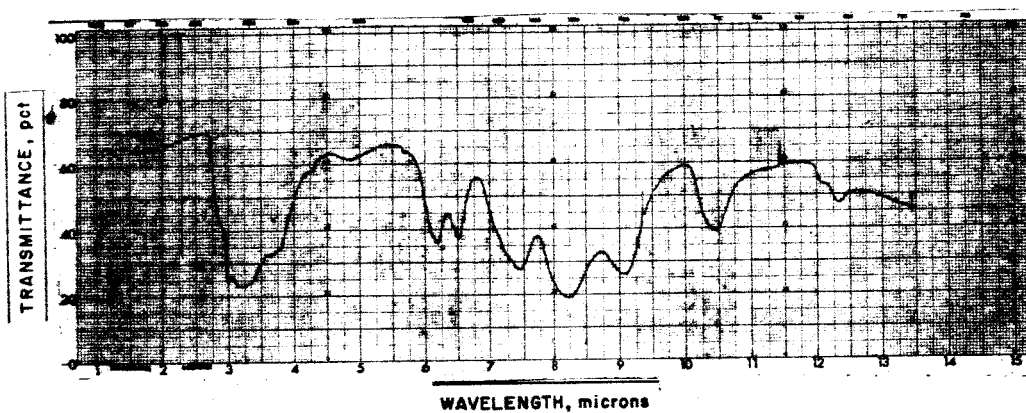


FIGURE 7. - Infrared Spectrum of Reaction Product in 2-D Engine Test; A-50/NTO (KBr Matrix).

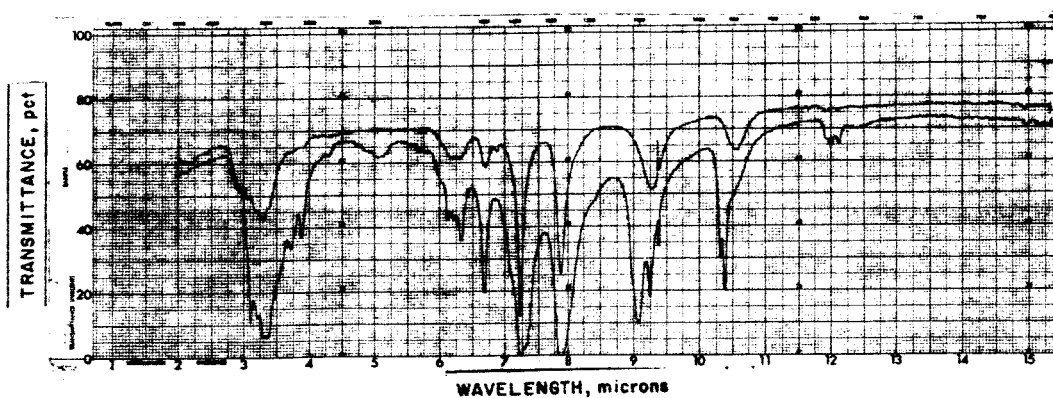


FIGURE 8. - Infrared Spectrum of Reaction Product in 2-D Engine Test; A-50/NTO (Liquid Phase).

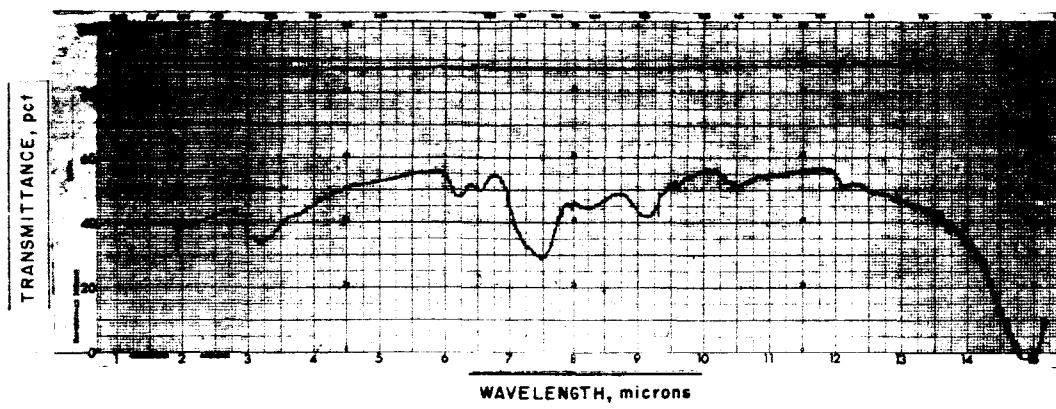


FIGURE 9. - Infrared Spectrum of Reaction Product in 2-D Engine Test; $N_2H_4/NT0$ (Liquid Phase).

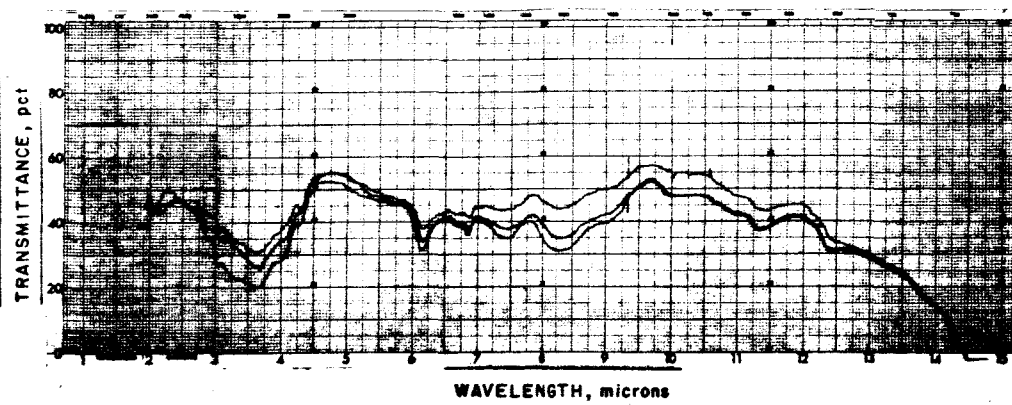


FIGURE 10. - Infrared Spectrum of Reaction Product in 2-D Engine Test; $MMH/NT0$ (Liquid Phase).

As explained earlier, the small amount of residue deposited on the 2-D engine walls was one of the major reasons for continuing these studies in a flow reactor. Typical concentrations of total nitrates formed in the engine residues, as percent of total nitrates possible (eq. 65) were: N_2H_4 , 2.4 pct HN; MMH, 1.2 pct MN; UDMH, 1.6 pct AN; and A-50, 2.0 pct HN; these values are the averages of four experiments. These low yields are primarily believed to be attributable to the fact that first, most of the condensed reaction products exhausted through the engine nozzle together with the gaseous products; and second, stream separation of the impinging propellant jets reduced the probability of reaction and, hence, the yield. The one-on-one-unlike injector used in the engine runs results in poor mixing under vacuum startup conditions, and minimizes the extent of reaction.

Although nitrates were the major constituents found in the engine residues, the presence of other compounds was carefully considered. It had been previously speculated that azides (hydrogen azide, fuel azide or methyl azide) could form under the conditions found in the engines. The spectra of all the residues obtained in the 2-D engine runs were scanned for evidence of azides and a few showed small peaks at 4.0 microns, indicating the azide ion. These peaks were observed in both N_2H_4 and A-50 runs but not in MMH or UDMH runs. Clark (66) notes that monosubstituted hydrazines, when reacting with specific oxidizers, form azides (eq. 55). Koehler and his coworkers (67) reacted UDMH with NTO at very low pressures and detected a covalent azide, which they suggested was methyl azide. Water, which is inevitably present in all the reaction products of these propellant combinations, has an absorption peak in the same region as the azide ion; but its peak is usually broad while the azide peak is narrow and sharp. Nonetheless, the presence of water interferes with the detection of the azide when the latter is present in small amounts.

The infrared spectra were useful in identifying the reaction products; but insight into the reaction intermediates and through them into the reaction mechanism also was sought. It was anticipated that the samples collected on the low-temperature sampling device would yield some additional information. These samples could be analyzed with either the infrared spectrophotometer or a differential scanning calorimeter. The latter was chosen because it required no further preparation of the collected sample prior to the analysis.

The material found on the sampling device was mostly unreacted propellants and occasionally water, suggesting that reactions in the 2-D engine tests take place on the engine walls. These results were not completely unexpected. Although the engine was evacuated prior to each test, as soon as the hypergolic propellants were injected into the engine, pressures of 0.35 to 0.4 atm were recorded and, at times, they were as high as 1.4 atm. These pressures, higher than the vapor pressures of the individual propellants, were sufficient to prevent complete vaporization of these injected propellants.

It was expected that nonreactive liquid streams, sprayed into the combustion chamber, would cover the wall with a film; while reaction products of vapor-phase reactions would deposit on the walls in the form of droplets, formed on available nuclei or on "active" sites on the walls. Indeed, in tests in which only one of the propellants, either fuel or oxidant, was injected into the 2-D engine, continuous films covered the walls, for however short a time. High-speed photography of the 2-D engine tests, which recorded the continuous films, clearly showed when propellant combinations were injected simultaneously, that stream separation occurred. Apparently, stream separation caused the deposition of unmixed propellants in the form of fine mist on the walls. Stream separation phenomena, which is an important factor in engine behavior, is extensively discussed in the literature, and references to it can be found in volume I.

In Bureau tests in which nonexplosive ignitions took place, it was established that the ignitions had no apparent effect on the final products accumulated in the engine. Takimoto and Denault (68), on the other hand, found that nonvolatile deposits accumulated in their low-pressure engine tests only when flameless reactions occurred.

Twice within this series of 2-D engine experiments, an explosive ignition occurred, breaking the engine both times with initially clean engines; in both cases the fuel was N_2H_4 . A white powder found on the broken wall fragments following one of the explosions was free of nitrate; unfortunately, the composition of this powder was not further established. The fact that the engine was clean at the onset of injection is important. It has been suggested that only when enough potentially explosive residue accumulated on the walls of the engine would a hard start take place. Also, in all their testing, MSC never found a hard start to occur in a clean engine. Moreover, since a nitrate residue was not found on the broken walls of the engine in contrast to nonexplosive experiments whose residues always contained some nitrate, it is suggested that the nitrate formed in the run was consumed in the explosion, and even if it was not the specific cause of the explosion, it served as added fuel for it.

Many other researchers have conducted tests in various engines, and some of their results are presented in this section. Takimoto and Denault (68), whose work was cited earlier, used MMH as the fuel. They employed a pulse-mode Marquardt, 22-lb thrust engine, and a 1-lb thrust engine fired

under either steady-state or pulse-mode conditions. The material they collected in the large engine was not determined precisely, but did not appear to be MN. The residue from the steady-state firing of the small engine contained mostly AN, while the residue from the pulse-mode firing of the small engine contained mainly MN and small amounts of a second material, which Takimoto (68) suggests is monomethylhydrazine dinitrate (M2N) or possibly a nitro or nitroso derivative. This is the only known instance where AN is reported as a product of the MMH/NTO reaction. Since an engine firing under steady-state conditions reaches higher temperatures than one which is fired in pulse-mode, and since MN is temperature-sensitive, it is probable that the higher temperature of the steady firing converts the MN, initially formed, to AN. Therefore, the higher engine temperatures are beneficial to the lessening of hard-start problems as pointed out by Juran and Stechman (69), who claim that when pulsed rocket engines are tested under altitude conditions, the probability of large ignition overpressures generally decreases as the temperature of the rocket engine increases. Juran and Stechman (69) believe that this trend suggests a relationship between ignition overpressures and accumulations of energy-rich substances on the internal surfaces of the engine. We have shown in volume III, that temperatures far higher than these reached in the engines, are needed for the evaporation and complete removal of HN residues. On the other hand, the conversion of heat-sensitive residues such as UN, MN, or H2N to a less sensitive explosive such as AN could easily be accomplished at lower temperatures and may be a factor in the overpressure problem.

In Juran and Stechman's (69) engine runs with A-50/NTO, they studied the effects of wall temperature, oxidant lead, number of pulses per run, and off-time between pulses. They concluded that the accumulation of residue--the amount of which is related to engine temperature and to engine position during firing (i.e., firing upward, downward, or horizontal)--caused explosions, and that oxidant lead was detrimental. These conclusions, in general, agree with those of other researchers.

Another engine study, conducted by Minton and Zwick (70), showed that pressure spikes of approximately 300 μ sec duration and as high as 200 atm, occurred prior to the establishment of the steady-state ignition pressure; in their tests, engine steady-state pressure corresponded to about 7 atm. Not always was the first pressure peak higher than the following ones, as suggested by some. The repetitive spiking continued for six or more cycles before reaching steady state.

Minton and Zwick (70) found that the frequency and magnitude of these spikes displayed a wide, random distribution, indicating that either the ignition process is composed of many parts each with its own accumulative variance, and/or that one or more steps are sensitive to extremely small disturbances (for instance, the spreading and mixing of the injectants may be sensitive to the surface finish of the injection orifice). Minton and Zwick (70) employed a combustion engine machined from clear plastic to observe the ignition processes, and could actually see regions of contact

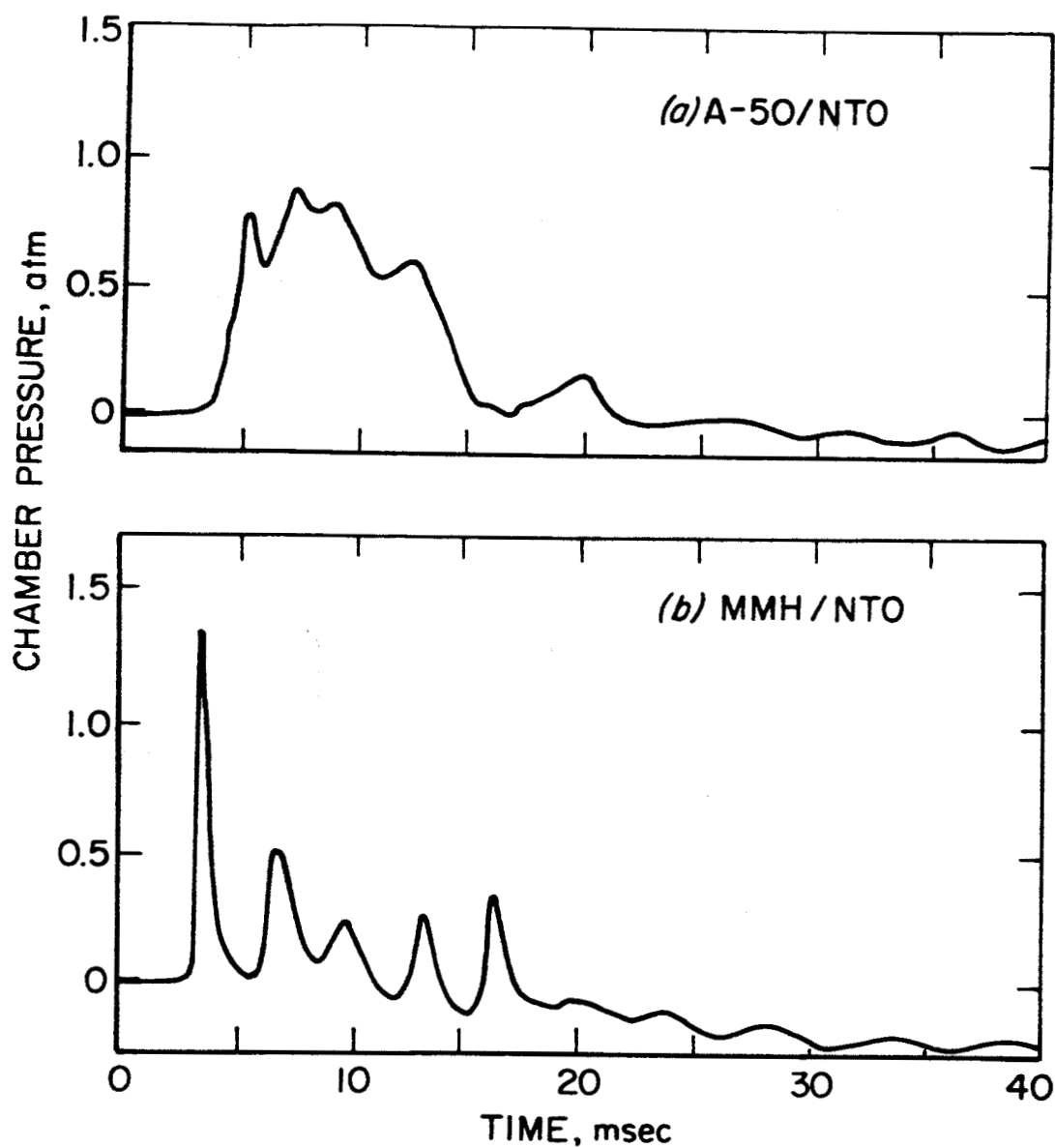
between fuel and oxidant, especially in lead-lag runs. Formation of a luminous area, which then spread slowly through the engine, was signified by them as the initiation of ignition. The usual progression of the reaction front inside the engine took about 1.0 msec, while during hard starts it took about one-third of a millisecond. Minton and Zwick (70) and Kappel and Knox (71), in a related study, present a detailed analysis of all the possible mechanisms of explosion and detonation that they hypothesize.

Although most of our experiments were concerned with the preignition period, some postcombustion analysis also was conducted. Figure 11 shows two typical chamber pressure records of postcombustion experiments for the two propellant combinations A-50/NTO and MMH/NTO using 0.25 ml of both fuel and oxidant in each test. The oscillatory behavior of the pressure is characteristic of the shutdown transient of these engines and results from the close coupling of the chamber pressure and the low injection pressure. In the case of the A-50/NTO combination, the chamber pressure peaks in about 5 msec, whereas in the MMH/NTO run it peaks in less than 3 msec. These rates of pressure rise are in agreement with the relative rates of vaporization of A-50 and MMH.

SUMMARY

The 2-D engine experiments indicated that the residue-forming reactions probably occur on the engine walls; the residues consist mainly of dilute aqueous salt solutions or of salt solutions in unreacted propellant. The salts formed depended on the fuel used as follows: HN in N_2H_4 runs, MN in MMH runs, HN in A-50 experiments, and AN in the UDMH experiments. Takimoto and Denault (68) found AN and M2N in MMH/NTO engine experiments under steady state firing conditions at which higher temperatures prevailed in the engine. The deposits on the low-temperature sampling device were either unreacted propellant or water, suggesting that reactions occur on the engine walls.

Azide peaks were detected in the liquid residues from N_2H_4 and A-50 runs. Many of the nitrate salt solutions with their respective parent fuels are sensitive explosives, as are solutions containing azides. Thin wall films of these solutions can be initiated to detonation. In several instances, clean engines exploded immediately following injection of the propellants. In these cases, residue is certainly not the cause of the explosion. We believe that these are gas-phase detonations of the fuel/NTO mixtures. Although the pressures attained in these detonations were large enough to break the plastic 2-D engine, they were not large enough to break the RCS molybdenum engines. This fact was ascertained when a stoichiometric ethylene/oxygen mixture, initially at 1 atm pressure, was repeatedly exploded in an RCS molybdenum engine without visible damage.



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FIGURE 11. - Postcombustion Chamber Pressure Histories, Obtained for: (a) A-50/NT0 and (b) MMH/NT0 Runs Using 0.25 cc of Fuel and NT0 with a 0 msec Fuel-lag.

Pressure peaks as high as 200 atm with 300 μ sec durations were measured by Minton and Zwick (70) in engines during the ignition process. The fine structure in these pressure records could be explained as a gas phase detonation that is reflected off the walls and reverberating inside the engine.

PROPELLANT REACTIONS IN THE GAS PHASE FLOW REACTOR

Introduction

A gas phase flow reactor facility was designed to generate larger quantities of reaction products than could be produced in the 2-D engine. Use of the flow reactor was also advantageous in that it provided a means for studying the temporal nature of the reactions. It had been previously demonstrated that the major 2-D engine preignition products were similar to those formed in the flow reactor and, based partly on these results, the flow reactor study was undertaken as an additional part of the Bureau's experimental program related to the chemistry of the hypergolic propellants in the engine.

Experimental Apparatus

A diagram of the basic features of the flow reactor is shown in figure 12; during the course of the program the system was modified to accommodate changing requirements.

In all the experiments, the fuels were metered as liquids and vaporized prior to introduction into the reactors; NTO was metered as a gas directly from the reservoir. Plenum chambers were inserted in the vapor lines to suppress gas pulsations in the reactor, while a variable-area choked orifice, placed between the flow monitoring and the sampling sections, was used to prevent downstream pressure perturbations. As a double check on the propellant flow rates, samples of the two propellants (fuel and oxidant) were occasionally collected in liquid nitrogen (LN_2) cooled sample cells over a known period of time just prior to the initiation of the experiment and the volume collected was measured.

Initially the flow reactor was tubular and included Irtran-2⁶ sampling disks. The disks were located inside the reactor, along its vertical axis, approximately 5 cm apart in slotted glass sleeves that were slipped into the reactor prior to each run.

⁶See footnote 4 on page 8.

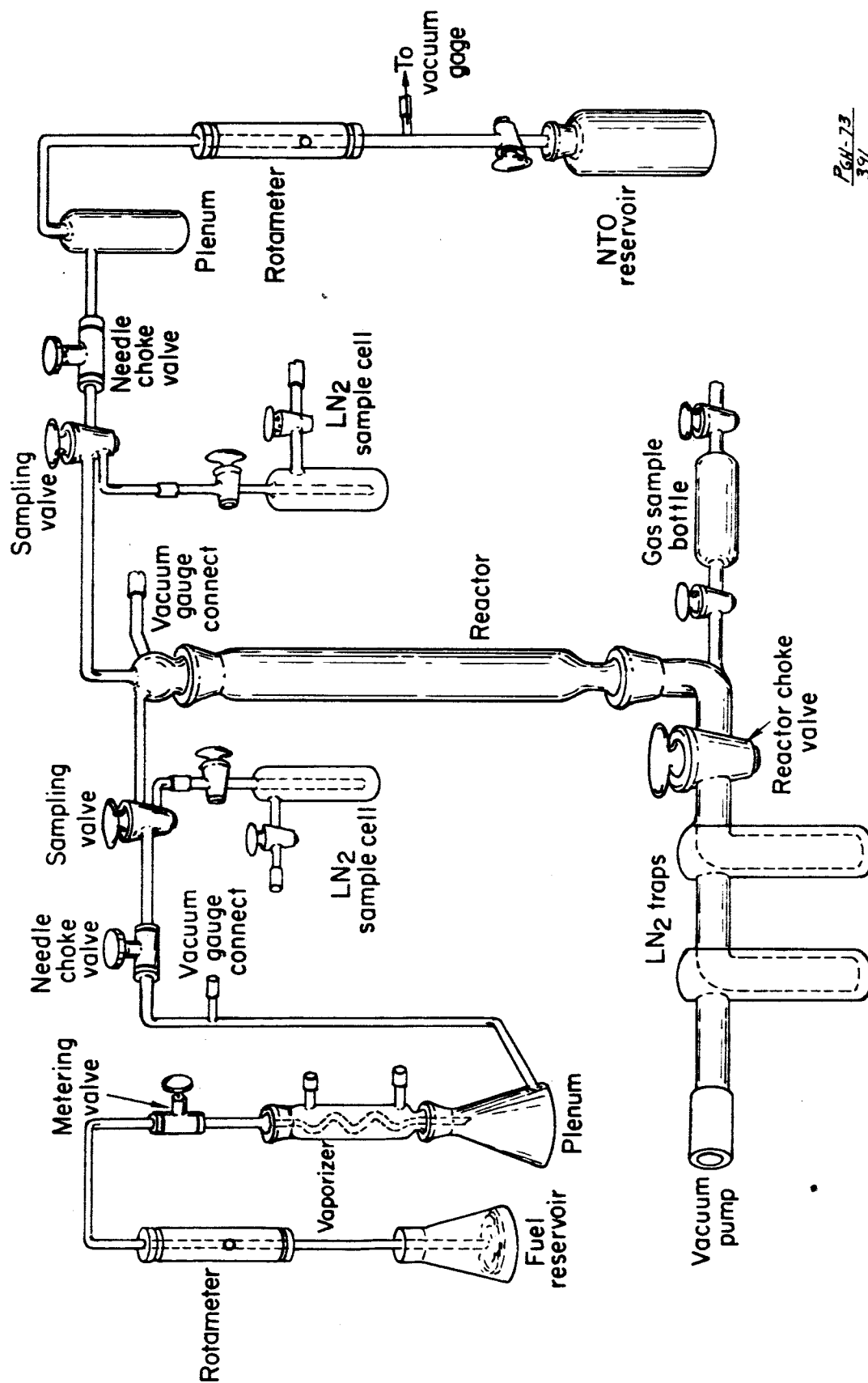


FIGURE 12. - Gas Phase Flow Reactor Apparatus.

A later version of the reactor section utilized a quartz tube of square cross section which had Irtran-2 windows in opposite sidewalls to permit continuous monitoring of the reaction, in situ, by an infrared spectrophotometer.

Gas sampling bottles were located downstream of the reactor to collect samples of the product gases during the runs for subsequent analysis. A 0.1-sec response low-pressure transducer monitored the reaction pressure, and leak valves were used for introducing known amounts of inert gases (helium and argon) into the reactors. The inert gases were added to provide an internal standard for the mass spectral analysis of the gaseous products and, when desired, for dilution purposes.

Experimental Procedure

All parts of the flow reactor were thoroughly cleaned before each run and then assembled. In some of the runs, all internal surfaces were pre-treated with N_2H_4 and then recleaned. After evacuation of the flow reactor to a pressure not higher than 10 microns Hg and the establishment of the desired steady flow into the LN_2 sampling dewars, the propellants were directed into the reaction chamber and the reaction commenced. At the onset of the reaction, a very fine powder-like translucent deposit collected on the reactor walls near the point of stream impingement, and as the reaction proceeded, the deposit moved down the reactor covering all available surfaces until it reached the bottom of the reactor. At this time, the main reaction was stopped by discontinuing the propellant flows.

During the reaction, the gas sampling bottles were opened for short periods of time to admit gaseous reaction products into the evacuated flasks. The remainder of the reaction product gases and the unreacted propellants were collected in LN_2 cooled traps downstream. When the tubular reactor was used, nitrogen or an inert gas such as argon or helium was introduced into the reactor at the end of the reaction until the system returned to atmospheric pressure, and the reactor could be opened. An inert gas gently flowed through the reactor after it was opened until the sampling disks were removed and samples from the reactor wall were collected.

Immediately after the sampling disks were removed from the reactor, they were covered with another, clean Irtran-2 window and then pressed together, by means of clips, in an infrared spectrophotometer sample holder.

These precautions--use of inert gas and cover disk-- were undertaken after analysis of reaction products of the first few tests indicated the possibility of incomplete reactions and the presence of unstable intermediates. The infrared spectra of the initial test products were unsatisfactory; improved spectra were obtained from the two-disk arrangement.

Reaction products deposited on the walls of the reactor were also analyzed. The products were removed from the wall with KBr powder. The powder was dusted onto the reactor walls, adsorbed the liquid on the wall, and was then shaken out of the reactor directly into a clean minipress in which it was pelletized for analysis in the infrared spectrophotometer.

Three fuels were used in these tests: N_2H_4 , MMH, and UDMH; lack of time prevented A-50 studies. In one UDMH/NTO test an explosion occurred in the LN_2 cooled product trap, which destroyed a large portion of the apparatus, while in another UDMH/NTO test a fast reaction, though nonexplosive, also transpired in the product trap.

Results and Discussion

Condensed Phase Products

In situ analysis of the reaction intermediates and products during the reaction was not successful. The very fine mist or powder which deposited on the windows produced interference bands in the resultant infrared spectra. The presence of water vapor obscured some of the details of these spectra; it absorbs strongly at 3 to 4 microns as well as at 6 microns, and has a broad and relatively strong absorption in the range of 9 to 15 microns. It also absorbs weakly around 475 microns. When aqueous solutions are analyzed, smaller path lengths than those in KBr disks must be used and this lowers the system sensitivity. An additional adverse effect is created by the broadening of the absorption bands in aqueous solutions compared with KBr disks (72). In general, identification of some materials in dilute aqueous solutions proves difficult. Figures 13 and 14 are infrared spectra of in situ scanning of reaction products.

Because of these problems the in situ procedure was abandoned, and reaction products were analyzed following the runs, after removal from the flow reactor. When the square reaction vessel was employed, the reactor filled with nitrogen was removed from the complete facility, immediately sealed, and inserted in the infrared spectrophotometer for analysis. The reaction products analyzed in this manner were exposed to the atmosphere only for a short time.

In some respects, experimental results in the flow reactor were identical to those in the 2-D engine. Specifically, nitrates were the major reaction products. As in the 2-D engine runs, the residues from the MMH runs consisted mainly of MN, as can be seen, for instance, in the infrared spectrum of the product in figure 15; while in the N_2H_4 runs, the nature of the nitrate depended on the O/F ratio.

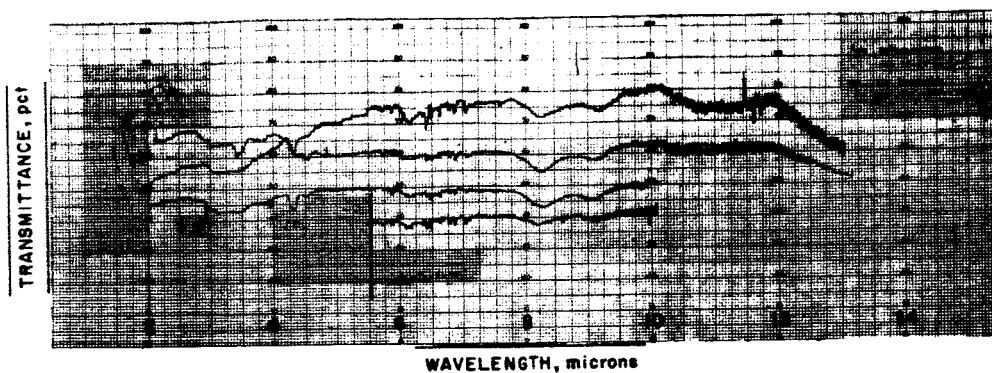


FIGURE 13. - Infrared Spectrum of Reaction Products of N_2H_4 /NTO/Argon Test, in Flow Reactor (in Closed Tube) (O/F = 0.21).

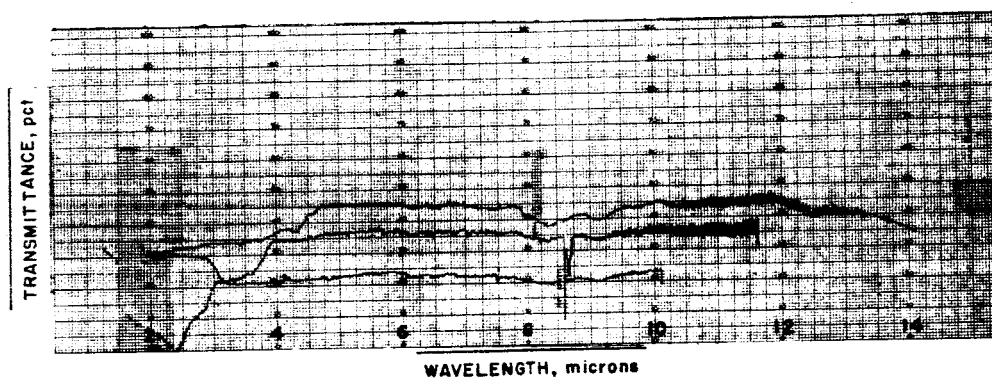


FIGURE 14. - Infrared Spectrum of Reaction Products of N_2H_4 /NTO/Argon Test in Flow Reactor (in situ) (O/F = 0.59).

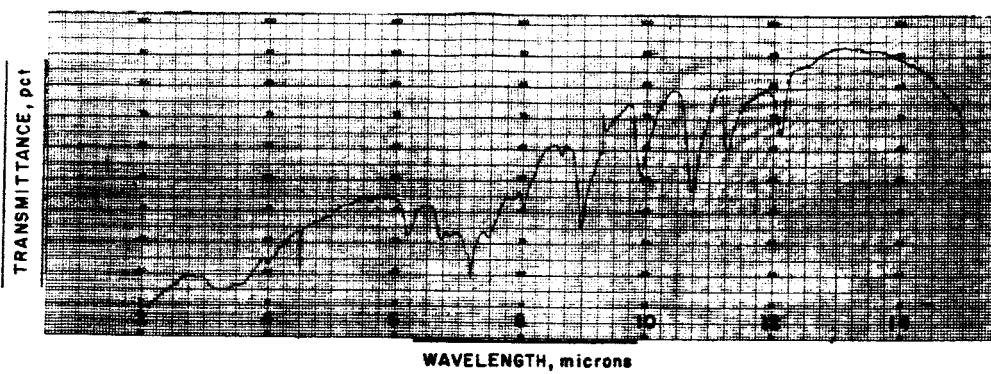


FIGURE 15 - Infrared Spectrum of Reaction Product
of MMH/NTO Test in Flow Reactor
(KBr Matrix)

UDMH experiments formed nitrates too, but these nitrates were not explicitly identified. For unknown reasons not enough product was obtained from most runs for a definite analysis. Figure 16 of a UDMH experiment in which oxidant was in large excess ($O/F = 7.2$) shows mostly potassium nitrate (KNO_3), due to the reaction of KBr with the unreacted oxidant; any other nitrate formed is obscured by the KNO_3 . The infrared spectrum of the residue of UDMH/NTO experiment in which the fuel was in excess ($O/F = 0.3$) is given in figure 17. The residue was collected from the bottom part of the flow reactor with loose KBr powder. A pellet pressed from this KBr powder gave the lowest trace (fig. 17). The shape of the trace and its location on the chart paper indicated that the sample was too concentrated, whereupon the sample pellet was divided into smaller portions and one portion was diluted with additional KBr and a new pellet was pressed from the diluted portion; the middle trace is the spectrum of this latter pellet and it shows the presence of nitrate other than AN, possibly that of UN. The diluted pellet was further broken down to give an even more dilute sample. This latest sample, prepared in the same manner as the other two, underwent three grinding and pressing steps; its infrared spectrum attests to this. Decomposition of the original residue material must have occurred during the preparation steps to yield a final infrared spectrum of AN only (upper trace). Thus, figure 17 shows some of the problems encountered in the analysis of the residues, especially when they contained temperature-sensitive products such as UN.

The spectrum of the product of a UDMH run, in which the oxidant was in small excess ($O/F = 1.3$) is shown in figure 18, in the upper trace, which is that of the product in a KBr matrix. In this trace can be seen, more clearly, the same peaks as in the center trace of figure 17; although the ratios of the different peak heights vary in the two traces. The nitration reaction, being a neutralizing reaction between an acidic and a basic compound, can be expected to yield the largest amount of nitrate with equal amounts of propellants (fig. 18).

The results of N_2H_4 experiments clearly indicate that the final nitrate product depended on the O/F ratio. In N_2H_4 -rich runs, ammonium nitrate (AN) was the major product. The spectrum of one such experiment ($O/F = 0.2$) is shown in figure 19. In addition to the infrared absorption peaks of AN, another major peak occurs in these spectra at approximately 7.87 microns, which is usually associated with the nitrite group. Considering the presence of excess N_2H_4 , this peak could be due to ammonium nitrite. Similar nitrite peaks were noted in the spectra of residues of runs with other fuels. For example, the spectrum of the residue from one MMH experiment contains, in addition to the main MN product, a peak at 7.9 microns (fig. 20). The O/F ratio for this specific experiment is not known. To say that either ammonium nitrite or monomethylhydrazine nitrite is present is speculative.

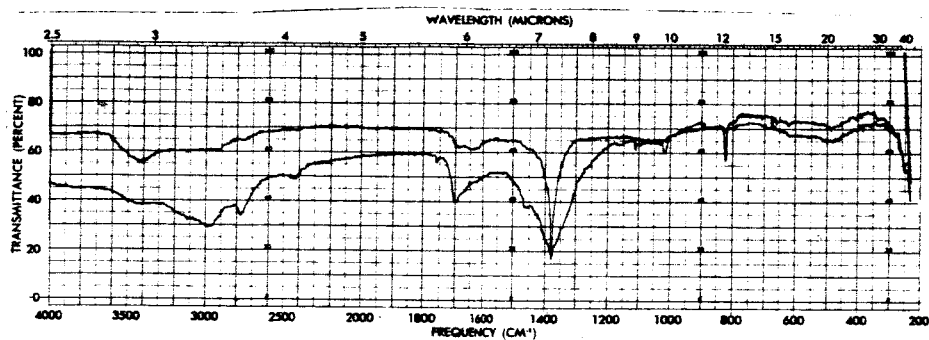


FIGURE 16. - Infrared Spectrum of Reaction Product of UDMH/NTO Test in Flow Reactor (O/F = 7.2) (KBr Matrix) (KNO₃).

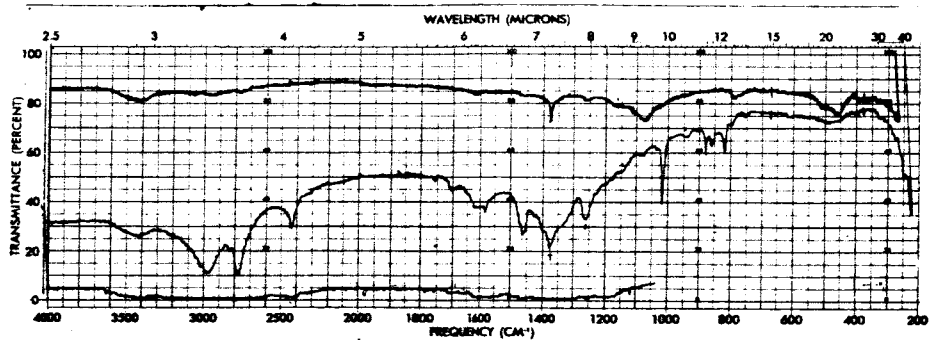


FIGURE 17. - Infrared Spectrum of Reaction Product of UDMH/NTO Test in Flow Reactor (O/F = 0.3) (KBr Matrix).

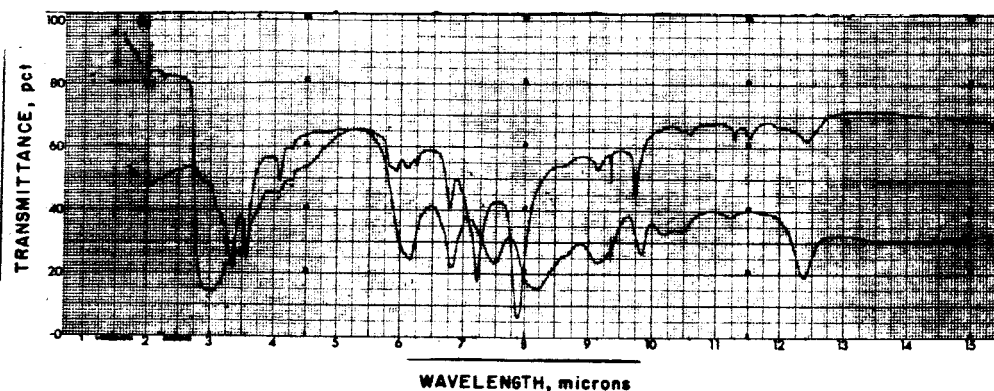


FIGURE 18. - Infrared Spectrum of Reaction Product of UDMH/NTO Test in Flow Reactor (O/F = 1.3) (KBr Matrix).

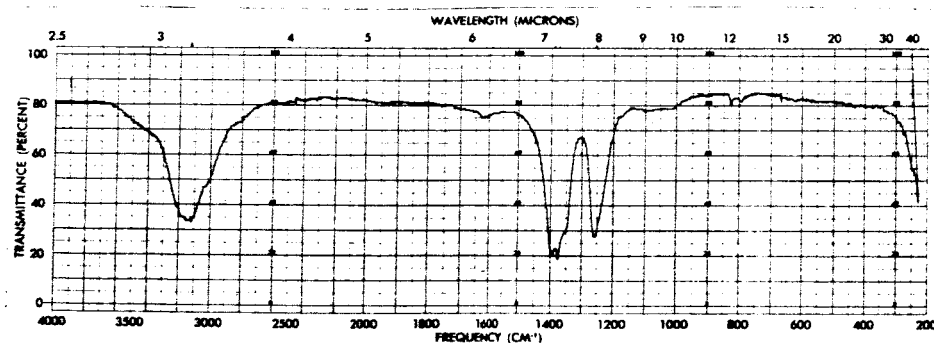


FIGURE 19. - Infrared Spectrum of Reaction Product of N₂H₄/NTO/Argon Test in Flow Reactor (O/F = 0.2) (KBr Matrix).

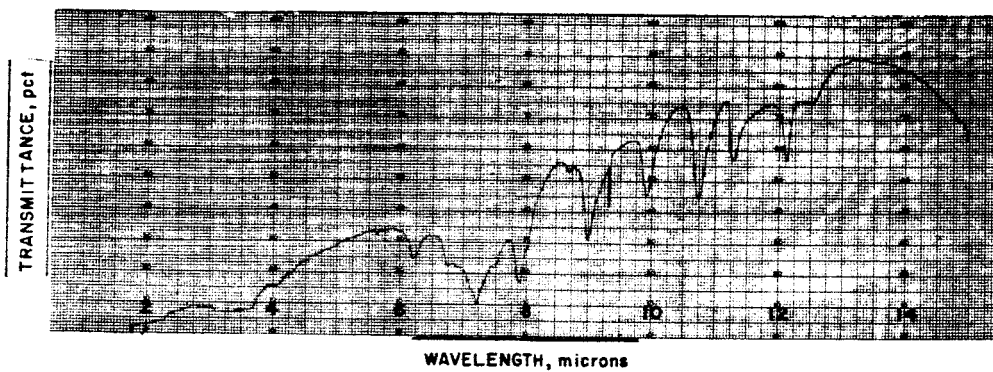


FIGURE 20. - Infrared Spectrum of Reaction Product of MMH/NTO (O/F Not Known) (KBr Matrix).

An example of the results found in NTO-rich experiments with N_2H_4 as fuel is given in figure 21, in which the infrared spectrum of HN is evident. The O/F ratio in this particular run was 7.8. Evident also is the presence of the nitrite ion at ~ 7.8 microns, which in the case of NTO-rich runs is indicative of unreacted, dissociated NTO. Mentioned earlier was the possible reaction of KBr with unreacted NTO to form KNO_3 . Another possibility in the oxidant-rich N_2H_4 runs was the formation of hydrazine dinitrate, which in turn could decompose to form HN and AN, among the products. The HN, if in much larger amounts than AN, will mask the presence of AN in the infrared spectrum somewhat. Thus, it would appear that the product of reaction was mostly HN, unless special attention were given to peak height ratios.

These experiments show the possibility of forming different reaction products, contingent upon the O/F ratio. It also is possible that other products could have been formed had a more detailed study of O/F ratios been undertaken.

In general, these results agree with those found by other researchers, although they vary in some particulars. The major difference is the formation of AN in N_2H_4 runs. In our runs, AN formed in excess N_2H_4 , while according to Ray and coworkers (73) and Zung and coworkers (74-75), AN formed when NTO was in excess. Specifically, Ray and coworkers (73) found that in excess N_2H_4 the major condensed product was HN; in slight excess of NTO, both HN and AN were found; while in greater excess NTO, the major product was AN.

There is no doubt that products of reaction between these propellants depend on the O/F ratio, temperature, and pressure, among others. Spatial and temporal dependence, mentioned earlier, have been suggested as the source of difference in the results. Depending on the mode of injection and the internal geometry of the reactor, pockets of fuel-rich and oxidant-rich solutions must have formed. Thus, sampling position is of utmost importance and is, of course, different in each case; this may explain the difference in results obtained by the various groups.

Seamans and Dawson (76) utilized a flow reactor in experiments using the MMH/NTO combination. An extensive chemical analysis of the residues showed the presence of unreacted MMH, MMH hydrate ($MMH \cdot H_2O$), MN, and $CH_3NH_3NO_3$ with the relative amounts of these compounds, depending among others on the initial O/F ratio.

In the flow reactor in which very low absolute amounts of propellants reacted, it is possible to have a constant O/F ratio at least in the gas phase. In the RCS engine (and in the 2-D engine and other experimental and test engines), the liquid streams of the two hypergolic propellants separate violently on contact; they must form pockets of varying O/F ratios and consequently the whole spectrum of products.

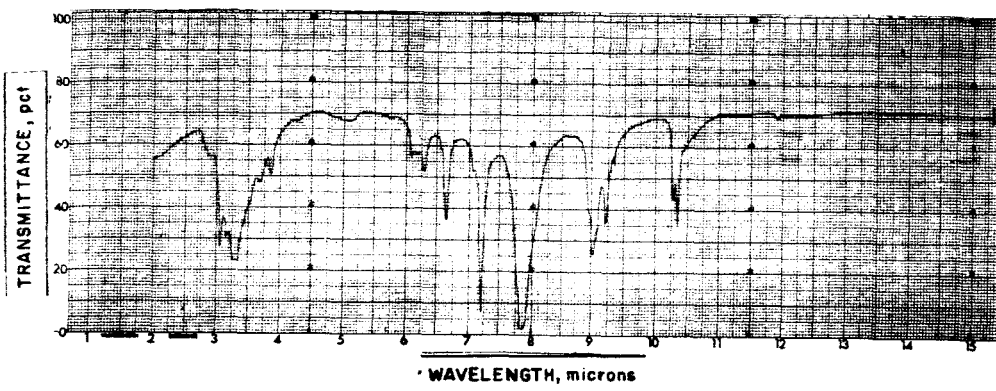


FIGURE 21. Infrared Spectrum of Reaction Product of $\text{N}_2\text{H}_4/\text{NTO}$ Test in Flow Reactor ($\text{O/F} = 7.8$) (KBr Matrix) (N_2H_4 Lead).

In this respect, the effect of the diluents also should be discussed. By changing the heat capacity of the system, the diluent may prevent or retard some reactions and, hence, results of experiments with diluents will present an incomplete picture of what occurs in the engine. Gray and Spencer's (44) study of UDMH reactions with O_2 , although not in an engine-type environment, did show that the reaction paths depended on O/F ratio, on diluent concentration and on volume-to-surface ratio, and could range from slow reactions to violent explosions. These reactions were even found to depend on the wall material. N_3H is known to substitute for the water in glass; NO_2 is known to form a monolayer on glass, at room temperatures and at low pressures (77). And Bowen and Birley (52), who studied the reaction of gaseous N_2H_4 and O_2 , found that peroxide formed on the glass vessel walls. It, therefore, is possible that certain reactions which take place on a glass surface will not take place on plastic or metal surfaces.

All the above is additional testimony that small changes in external conditions can result in significant changes in the course of reactions and in part may explain the different results found by the various research teams as well as the anomalous frequency of the hard-start phenomenon.

In one N_2H_4 /NTO experiment, with an O/F ratio of 0.54, the infrared spectrum of the products (fig. 22), appears to be that of hydrazine nitrite.

Intermediates of Reaction

During repetitious scanning of some of the products, certain peaks were found to diminish with, at times, the simultaneous appearance of new peaks and/or the enhancement of already present peaks. Specifically, the major disappearing peak was at about 8.3 microns, while the main nitrate peak at 7.5 microns was enhanced most often. This phenomenon was noted only in the liquid samples, not in samples that were prepared in a KBr matrix. Figures 23 and 24 present good examples of the phenomenon described. A closer look at the infrared spectra of products from the 2-D engine tests showed that this also occurred in the engine, as demonstrated in figures 25 and 26. Not only were individual samples scanned more than once; the various Irtran disks used in the flow reactor runs were scanned alternately with a variable scanning order. By this procedure, we found that not all the samples displayed the disappearing peak, and usually the first samples scanned exhibited the peak, while samples analyzed at a later time did not always show it distinctly. Figure 27 shows the scanning procedure in one of the N_2H_4 runs. The lowest curve with the pronounced peak was obtained first; while in the center curve, obtained last, the peak is almost gone.

This phenomenon suggests either of two things: (a) The presence of an unstable intermediate in the products, or (b) the presence of unreacted propellants on the sampling disks that react during the scanning period by the infrared beam, which takes place immediately following the pressing of the sample between the two Irtran disks. In the 2-D engine tests, pressures above those of the vapor pressures of the individual propellants were partly responsible for the deposition of unreacted propellants on the wall of the engine. Hence, both suggestions would seem to apply to the 2-D engine residues. In the flow reactor, the total pressure was much lower than the vapor pressures of the individual propellants, thus excluding condensation of the gaseous propellants, wherefore we are left with the unstable intermediate theory.

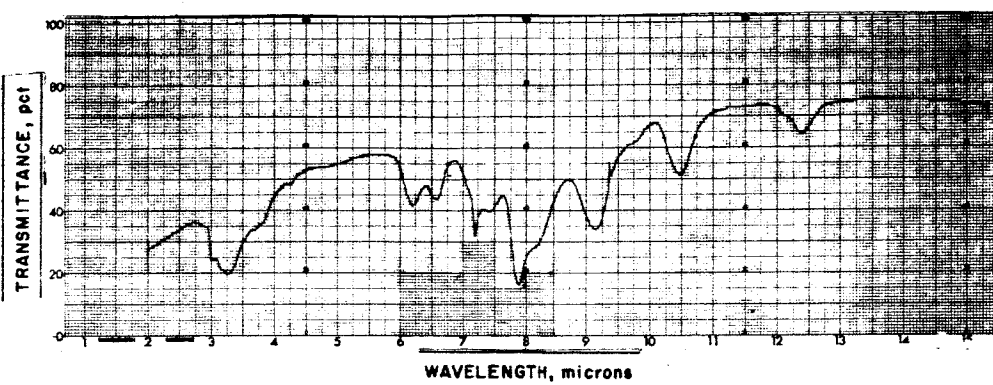


FIGURE 22. - Infrared Spectrum of Reaction Products of $\text{N}_2\text{H}_4/\text{NTO}/\text{Argon}$ Test in Flow Reactor ($\text{O/F} = 0.59$) (KBr Matrix) (Hydrazine Nitrite).

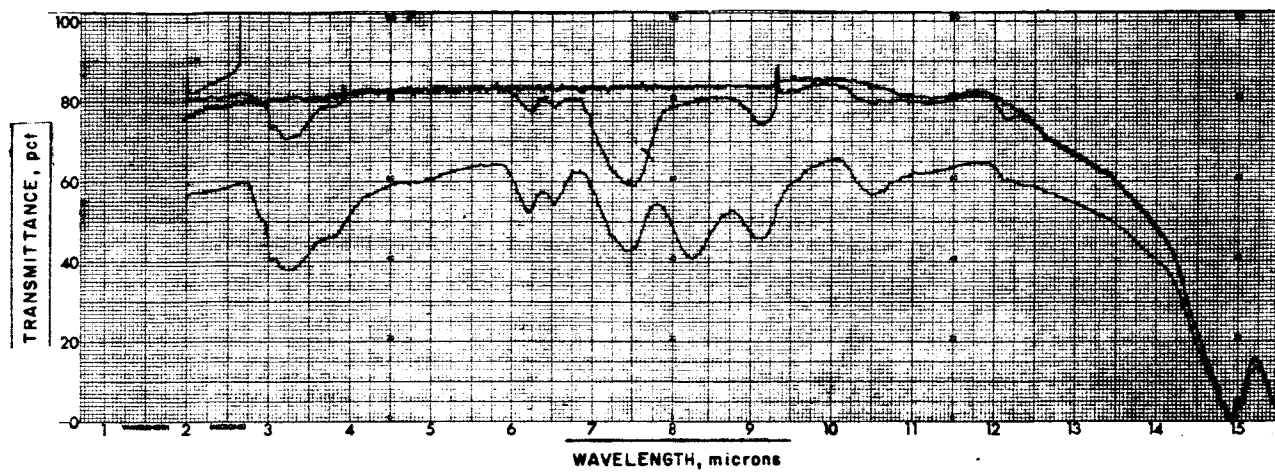


FIGURE 23. - Infrared Spectrum of Reaction Products of $\text{N}_2\text{H}_4/\text{NTO}$ Test in Flow Reactor ($\text{O/F} = 0.66$) (Liquid Phase).

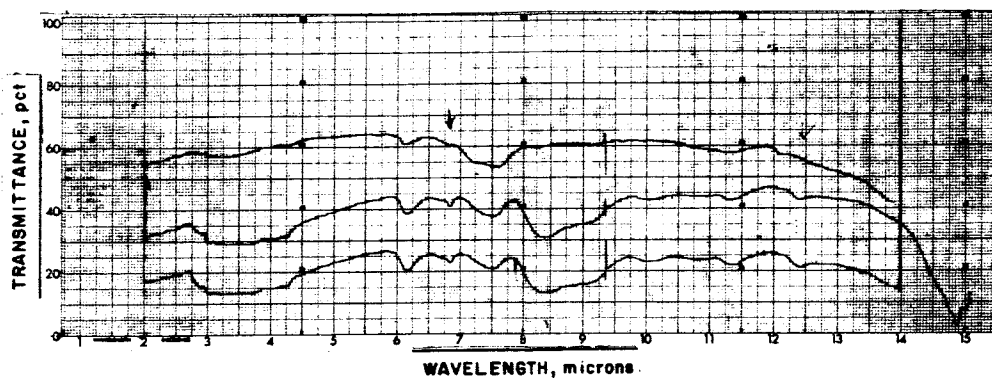


FIGURE 24. - Infrared Spectrum of Reaction Products of MMH/NTO Test in Flow Reactor ($\text{O/F} = 0.58$) (Liquid Phase).

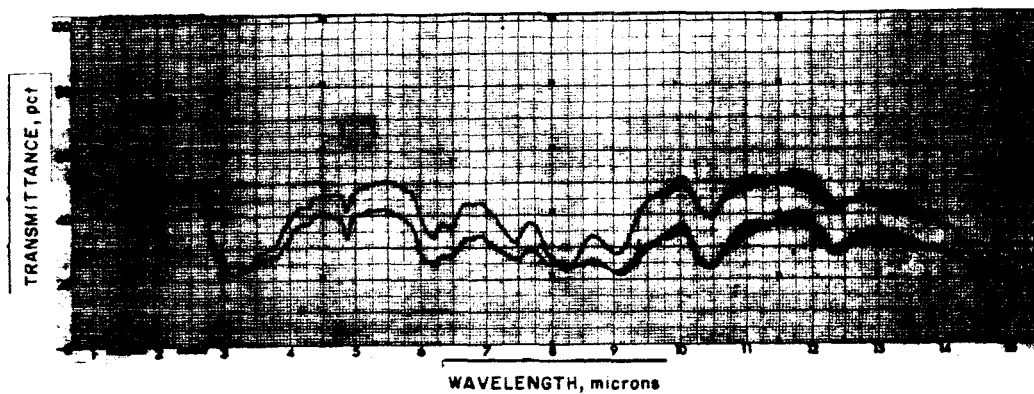


FIGURE 25. - Infrared Spectrum of Reaction Products of N_2H_4 /NTO Test in 2-D Engine (Liquid Phase).

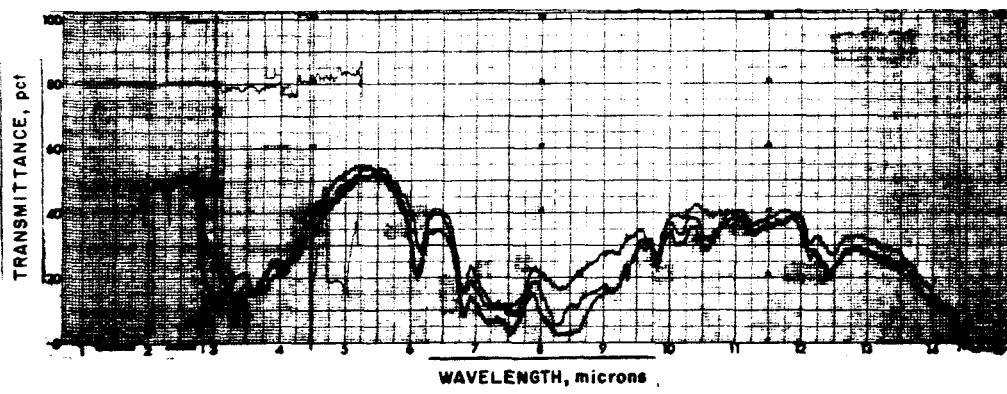


FIGURE 26. - Infrared Spectrum of Reaction Products of UDMH/NTO Test in 2-D Engine (Liquid Phase).

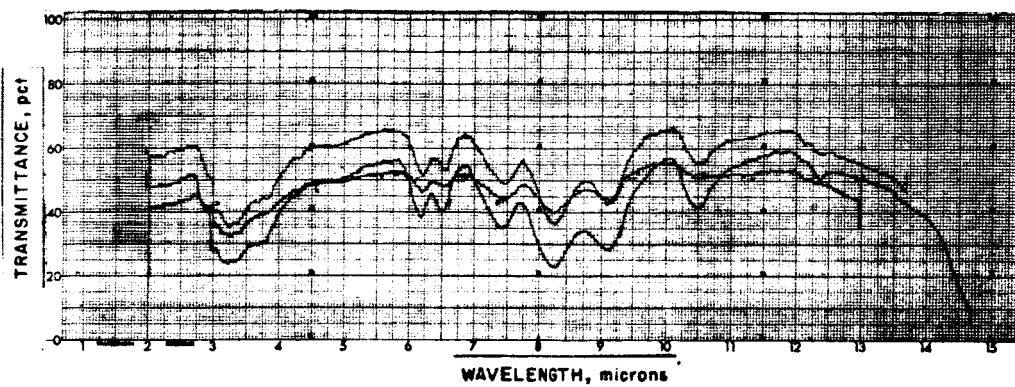


FIGURE 27. - Infrared Spectrum of Reaction Product of N_2H_4 /NTO Test in Flow Reactor ($O/F = 0.84$).
Top Curve: Sampling Disk No. 6 (done second);
Mid Curve: Sampling Disk No. 9 (done last);
Low Curve: Sampling Disk No. 2 (done first) (Liquid Phase).

At the low concentration and low temperatures prevalent in the flow reactor, the intermediate is relatively stable; scanning times suggest that it converts to the nitrate in about an hour. The position of the sample in the infrared spectrophotometer is very close to the focal point of the infrared beam. A temperature rise of about 15° C, and the infrared radiation may hasten the conversion of the intermediate.

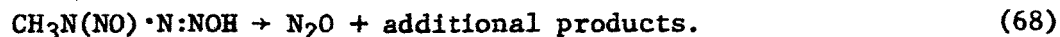
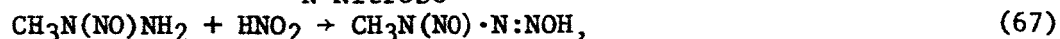
The intermediate was not detected in samples that were prepared for analysis in a KBr matrix. The preparation of a sample in KBr involves grinding and pressing operations which probably contribute to the decomposition of this material.

Thought has been given to the nature of the intermediate although techniques to preserve it, for example by freezing, so that it could be analyzed in detail, were not attempted. It was suggested (78) that the nitrogen-oxygen semipolar bond, $=N \rightarrow O$, a relatively unstable grouping, with an absorption band that can vary between 6.7 and 10.5 microns may be responsible for the intermediate. The exact locality of the absorption band for this semipolar bond depends on the substituted groups close to it; strong electron donors lower the frequency appreciably.

When samples on the sampling disks were not covered, vaporization of the product—concurrent with peak disappearance—did sometimes occur. Figure 28, which is a repeat scan of the top curve of figure 27, shows clearly the diminution of all the peaks of the spectrum, but for the nitrate bond at 7.5 microns. It is known (79) that when primary and secondary nitroso ($-N=O$) compounds volatilize, changes occur in their spectra. When these changes are observed by infrared spectrophotometry, it is seen that the bands of the nitroso compounds rapidly diminish in intensity on standing and new bands appear. In general, the $-N=O$ absorption appears to be particularly sensitive to the nature of its environment and to the neighboring chemical bonds.

Here, then, is possible indication that the nitration reaction proceeds via a nitroso intermediate, when the reaction takes place at low pressure and at a low concentration. The absorption frequencies of the nitroso and of the related N-nitroso (or nitrosamines ($-N-N=O$)) fall in the same range, as cited for compounds having the semipolar bond $=N \rightarrow O$.

Nitrous acid (62) attacks the secondary nitrogen atom in alkyl hydrazines to give an N-nitroso compound, which is a relatively stable crystalline compound. Further action by the acid gives an unstable aliphatic compound that stabilizes by losing nitrous oxide. Reactions are as follows:



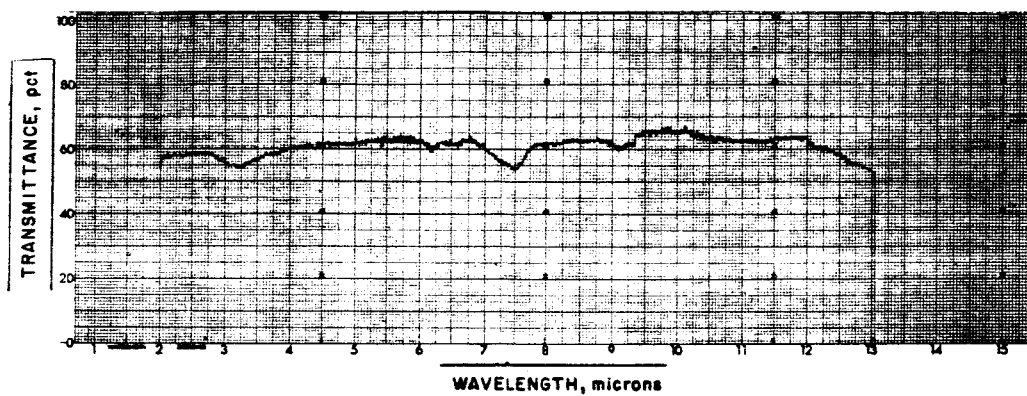
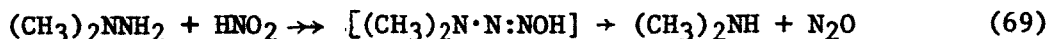


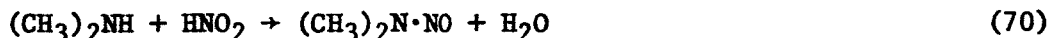
FIGURE 28. - Infrared Spectrum of Réaction Product of $\text{N}_2\text{H}_4\text{NTO}$ Test in Flow Reactor ($\text{O/F} = 0.84$). A repeat scan of sampling disk No. 6 (fig. 27).

Here is additional indication that, at times, the nitration reaction may proceed via a nitroso intermediate. The oxidation scheme of UDMH is more complex and depends strongly on the oxidizer. Oxidation by HNO_2 can form a secondary amine:

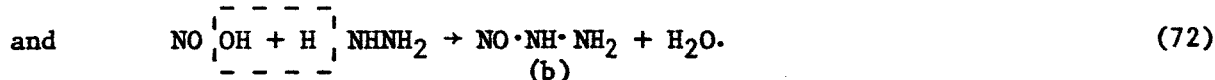
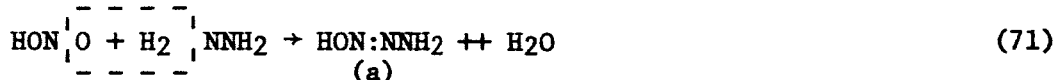


or more often the symmetrical tetramethyltetrazene (TMT).

The dimethylamine can further react with HNO_2 to form nitrosamine,



which, in turn, can undergo additional oxidation by a strong oxidant to yield a nitrite, $(\text{CH}_3)_2\text{NNO}_2$. The lower nitrosamines such as $(\text{CH}_3)_2\text{N}\cdot\text{NO}$ are volatile, water soluble liquids, as were our products. The reaction of N_2H_4 with HNO_2 may also form intermediates with a nitroso bond as in (b) below:



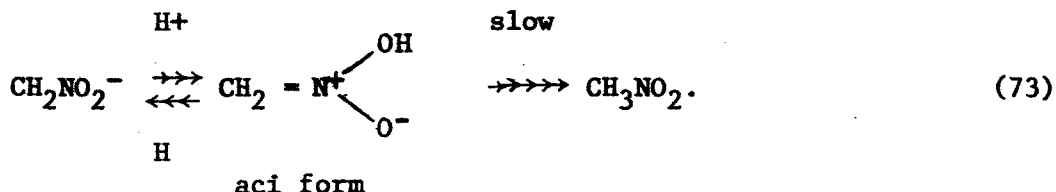
Derivatives of (b) are known (80).

The alkyl nitrosohydrazines, when heated in inert solvents, give off nitrous oxide and the corresponding amines in a similar way to that shown in equation 68. Although the degree of heating of a sample in a spectrophotometer by the infrared beam is not large, we have measured an elevation of 15°C above that of room temperature in samples being scanned in the Perkin-Elmer model 521 spectrophotometer.

The presence of nitroso or N-nitroso compounds in N_2H_4 , MMH, and UDMH products is possible, and it may be that the relatively slow changes that we see in the infrared spectra are due to the above reactions. A suggestion for the presence of nitroso compounds is elicited by McLain's results (81). His residues from MMH/NTO engine experiments, initially yellow brown, turned a dark aquamarine, after a period of several days, possibly by absorption of water and subsequent dilution. Tertiary aliphatic nitroso compounds are blue or green colored in dilute solutions, while colorless or yellow in more concentrated form. The color changes are due to dimerization through nitrogen-nitrogen bonding.

It is of interest that many types of bonds between N and O are relatively unstable and undergo slow reactions under the effects of heat or various solvents. Some of the compounds in the products may have these bonds.

An example of another material that undergoes slow change and may be present in the residue is nitromethane. Nitromethane has been identified as one of the reaction products of MMH/NTO reactions (82). A salt of nitromethane in an acidified solution forms an unstable, rather strongly acidic isomer of nitromethane called the aci form, which slowly reverts to the more stable nitro form (83) by the mechanism:



N_2H_4 in a mixture with nitromethane increases the tautomeric aci form of the nitromethane relative to the nitro form; it strongly sensitizes the nitromethane to detonation (84).

Seamans and Dawson (76), whose study of the MMH/NTO reaction was referred to earlier, found that the relative amounts of the compounds in the reaction products depended on the gradual decomposition of the compounds, due to the time lapse between the formation of the products and subsequent analysis. In samples that were analyzed long after their formation, an additional compound, methylhydrazinium-N-methyl-carbazate ($\text{CH}_3\text{N}_2\text{H}_2\text{COON}_2\text{H}_4\text{CH}_3$), was also detected. Here then is further evidence, not only to the importance of the initial O/F ratio to the final product, but to the importance of the analysis time of the reaction products and its effects on the interpretation of results.

Gaseous Products

The product gases from the flow reactor experiments were analyzed in a mass spectrometer; they consisted mainly of N_2 , NO , NO_2 , N_2O , NH_3 , H_2 , and O_2 with small quantities of CO and CO_2 (for substituted hydrazine fuels). Tetramethyltetrazene (TMT) was found in the UDMH experiments. Table 1 shows the percent concentration of the various product gases in N_2H_4 runs, and table 2 gives similar results for UDMH and MMH experiments. From the values for NO_2 given in table 1, it is apparent that the O/F ratio corresponding to a stoichiometric mixture for the N_2H_4 /NTO reaction lies between 0.79 and 3.0. Furthermore, the oxidant-rich system favors the formation of NO ; while the fuel-rich system favors NH_3 . Earlier Bureau studies (85) suggested the following reaction:

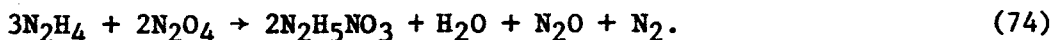


TABLE 1. - Products found in two samples taken from the low pressure
N₂H₄/N₂O gas reaction for various O/F ratios

Reactant O/F ratio	Sample ¹	N ₂ O	O ₂	NO	NH ₃	H ₂ O	N ₂	N ₂ H ₄	NO ₂	H ₂	Mean reaction pressure, microns
3.0	A	17.7	2.1	31.8	0.0	13.5	15.0	0.5	19.3	0.3	530
	B	11.1	7.6	12.5	.0	8.3	31.7	.2	28.3	.0	
0.79	A	12.8	5.7	23.4	.0	22.9	32.3	.0	.0	1.0	500
	B	11.3	3.3	37.9	.5	11.6	28.1	.2	5.4	.3	
0.76	A	19.6	1.5	4.9	18.8	20.3	34.8	.0	.0	.0	500
	B	9.6	5.3	3.2	13.6	27.7	40.6	.0	.0	.0	
0.59	A	10.0	8.9	7.1	8.5	29.0	36.0	.2	.0	.3	500
	B	6.6	1.3	30.0	4.4	29.0	27.7	.1	.0	.9	
0.21	A	2.0	14.9	1.6	4.7	7.6	66.6	2.6	.0	.0	350
	B	3.5	12.1	11.9	2.7	15.9	51.5	.0	.0	.0	

¹Samples A and B were taken at the beginning and end of each run, respectively.

TABLE 2. - Products obtained from two samples taken from the
low pressure UDMH/N₂O₄ and MMH/N₂O₄ reactions

Reactant		Sample ¹	N ₂ O	O ₂	NO	H ₂ O	N ₂	Fuel	NO ₂	H ₂	NH ₃	Mean reaction pressure, microns
Fuel	O/F											
UDMH	7.2	A	4.9	0.0	45.5	16.9	28.1	0.2	2.1	0.0	0.0	150
		B	-	-	-	Sample lost		-	-	-	-	
UDMH	1.3	A	3.0	3.8	45.1	19.2	18.8	.2	8.9	.2	.0	200
		B	2.1	10.1	25.0	14.3	42.3	.6	3.2	.0	.6	
UDMH	0.28	A	6.1	.0	7.0	7.0	15.0	50.0	1.4	.0	1.3	1,200
		B	7.7	7.0	4.6	11.0	42.0	24.0	0.7	.0	.8	
MMH	.58	A	1.3	6.2	1.7	8.2	49.1	28.5	.0	.0	.0	340
			-	-	-	No sample		-	-	-	-	

¹Samples A and B were taken at the beginning and end of each run, respectively.

However, the values in table 1 do not justify this choice for the reaction because the gases N_2O , H_2O , and N_2 are not present in the same proportions. As for the relative concentrations of NO , NO_2 , and O_2 , they depend greatly on pressure and temperature and not on the reaction mechanism between N_2H_4 and NTO . The large amounts of O_2 found in some of the samples are puzzling. One source of O_2 could be the nitrate itself. Molten nitrates of metals decompose via various paths forming nitrites, oxides, or the pure metals. Along with these products, N_2 , its oxides, and O_2 are also evolved. It is the liberation of O_2 which makes the molten nitrates strong oxidizers. The evolution of O_2 from nitrates is an endothermic process; it proceeds by itself only if the oxygen takes part in a process evolving more heat than is required to decompose the nitrate. Conditions for O_2 evolution are favorable if portions of the nitrate molecule react with O_2 which is to be split off with the production of heat. This occurs in AN (86). There is doubt, though, that all the O_2 in the gaseous reaction products originates in this manner. Whatever its source, since it is present together with NO , the two react to form NO_2 .

Similar preignition product delineation studies conducted by Zung, Lawver, and associates (74), using helium-diluted reaction mixtures gave product spectra similar to ours. Their results are given in table 3.

TABLE 3. - Gas product analysis and equilibrium temperature rises for argon-diluted N_2H_4 - NO_2 stirred reactions¹

Mole percent of each reactant.....	2.0	3.0	3.0	3.5	4.0	4.0	4.5	5.0	6.0
Temperature rise, ° C.....	109	238	237	315	468	542	606	737	843
Mole percent products:									
N_2O	0.70	0.24	0.22	0.16	0.29	0.16	0.10	0.23	0.24
N_2	1.68	3.79	4.13	5.15	6.06	6.92	2	7.98	8.75
NH_3	3	.25	3	.68	.23	.72	2	3	3
NO	1.66	3.93	3.78	3.79	4.39	2.80	2	3.16	4.73
H_2022	.11	.10	.21	.44	.91	2	.95	.61

¹From L. B. Zung, B. R. Lawver, E. A. Tkachenko, and B. P. Breen (74).

²Product analysis prevented by air leak into samples.

³No NH_3 present.

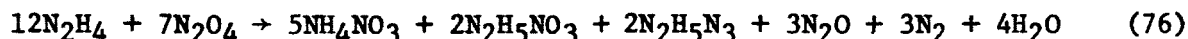
Zung and coworkers (74) concluded that the oxidant-rich gas phase reaction between N_2H_4 and NTO proceeded according to the reaction:



However, neither of these latter two reactions accounts for the large concentrations of NO and NH_3 observed in the products. In one of their runs, Zung, Lawver, and associates (75) reported 72 vol-pct NO; although, in general, the NO concentration ranged from 9 to 25 vol-pct, which agrees with the Bureau results.

Skinner, Hedley, and Snyder (12) studied the mechanism of homogeneous gas phase N_2H_4 /NTO reaction. Their tests were run with argon-diluted reactants. The molar O/F ratio was kept constant at 1, while the degree of dilution was changed. When the concentration of each of the reactants reached 5 mole percent, spontaneous ignition occurred; while below this concentration, preignition reactions proceeded. Although the O/F ratio was constant, the relative concentrations of the main gaseous products, N_2O , NO, and N_2 , varied with reactant concentrations. Below 2 mole percent of each reactant, N_2O and AN predominated. Above 2 mole percent, regular increases in N_2 and NO, at the expense of N_2O , resulted and finally at 3 mole percent of each reactant the amount of N_2O was minor. The results indicate a change in reaction mechanism with a change in absolute concentration of reactants. Comparison of these results with the results of the Bureau and those of Zung (74) is not simple. Due to the use of diluent and the higher total pressure in one system and the use of low pressures in the other tests, two factors which are important to reaction mechanisms are different, the number of active specie and the resultant total number of collisions occurring between them as well as the mean free paths for these collisions. These factors, among others, determine the mechanism and extent of reactions and explain partly the different results reported by the different researchers.

Ray, Koehler, and coworkers (73), who also studied the reaction using different O/F ratios, suggested the following reaction:



However, no substantial evidence is given to justify this reaction.

Neither the Bureau's (85) nor Zung's (74) condensed or gaseous reaction products show the presence of hydrazine azide or of other azides in any substantial proportions; rather the opposite is true. Of interest is the fact that the fuel-rich system favors formation of NH_3 , which would lead to the formation of AN, substantiating Bureau results.

Recently, Simoneit and coworkers (87) have obtained mass spectral analyses of the combustion products from the lunar module descent engine using A-50/NTO. The major reaction in this engine is probably the same as in the RCS attitude control engines when in steady state operation.

This engine can produce, continuously, large quantities of product exhaust gases, simplifying analysis and enabling the detection of gases usually found as traces. Of the total exhaust products, NH_3 , H_2O , CO , NO , O_2 , and NO_2 , comprised 88 pct; N_2 and CO_2 also were present in relatively large amounts. Acetylene, hydrogen cyanide, formaldehyde, nitrous oxide, propadiene, cyanous acid, nitric oxide, and formic acid were also found in smaller quantities. Many mass spectrometer m/e values not corresponding to the gaseous products shown in tables 1 and 2 were also found in the mass spectra of the gaseous compounds of our flow reactor products; they were not pursued further by us because the trace quantities of these m/e values precluded identification. These m/e values included the following: 57-60, 71-75, 81, 82, 91, 93, 105, 106, 120, and 134. Simoneit and coworkers (87) have collected the condensable exhaust products in cooled traps. Extracts of these frozen samples with methanol and benzene, analyzed with the high resolution mass spectrometer, were found to contain the following materials: Butadiene, 3-Hexan-1, 5-diene, hydrogen azide, methyl azide, ethyl azide, nitrilo hydrazine, nitromethane, ethylene, ketene, methylamines, and methyl nitrite among others.

The wide variety of the many complex materials reported in this study of the lunar module can be explained by the high temperatures reached in the exhaust products of this engine, leading to many polymerization reactions as well as to other types of reactions. Also, to reemphasize, many of the products could only be detected where copious amounts of gases form, as was the case in this study. Thus, although these results do not bear directly on the hard-start phenomenon or on the gaseous products collected in the flow reactions, they were cited here to illustrate the variety and breadth of the reactions possible with these propellants, and especially with an A-50 system.

Reaction products similar to those reported by Simoneit (87) were, at times, detected by other investigators, in engine, flow reactor, or laboratory scale experiments, and will be noted here briefly. Although the products were not specifically detected as gaseous compounds but as condensed phase products, their physical form is of no importance in this instance. Urry (34) studied the oxidation mechanism of UDMH and found among the oxidation products methyl azide, diazomethane, dimethylamine, dimethyl nitrosamine, and formaldehyde. Takimoto and Denault (68) did not detect methyl azide or diazomethane in the engine residues of the MMH/NTO reactions; nonetheless, they suggest these products as initiators of the more exothermic reactions occurring in the engines and attribute their absence to their high volatility. Mayer, Taylor, and Schieler (82) found the following materials in the preignition products of the MMH/NTO reaction at low temperature: Nitromethane, nitramide, and monomethyl nitramide. The products of this last study were different in that the low temperatures had an effect on the course of the reactions. Mayer (82) also observed the UDMH/NTO reaction and found the products to include mononitrodimethylamine. While reviewing this latter study (82), we also detected UN as a product in an infrared spectrum of the product of a UDMH/NTO reaction, which Mayer also studied. The spectrum is almost identical to that of a solution of UN

in UDMH prepared by the Bureau. The spectrum obtained by Mayer (82) is presented in figure 29. Since Mayer's study was done at both low concentration and low temperature conditions, the temperature-sensitive UN formed did not decompose and remained in the solution.

Summary

The gas flow reactor studies offered a choice of O/F ratios and showed the dependence of the nitrate products of the propellant reactions on these O/F ratios.

MN was found to be the main nitrate in MMH runs. In Bureau experiments, AN was formed under N_2H_4 -rich conditions while HN was formed under NTO-rich conditions. Larger amounts of NH_3 were also present in the N_2H_4 -rich experiments than in the other experiments. Possibly, N_2H_4 decomposed to NH_3 , which then reacted with NTO to form AN. The oxidant-rich runs show the presence of nitrite, suggested as indicative of ammonium nitrite. Other researchers are not in agreement with Bureau results, as regards AN and HN formation in N_2H_4 runs; whereas they found AN in NTO-rich runs and HN in N_2H_4 -rich runs.

An intermediate of reaction slowly decomposing into another product was observed during the scanning of product samples of the flow reactor as well as of the 2-D engine. The intermediate was not identified, but its behavior in the infrared beam and its absorption band suggest that it is a nitroso compound or a compound with the $=N\rightarrow O$ type bond.

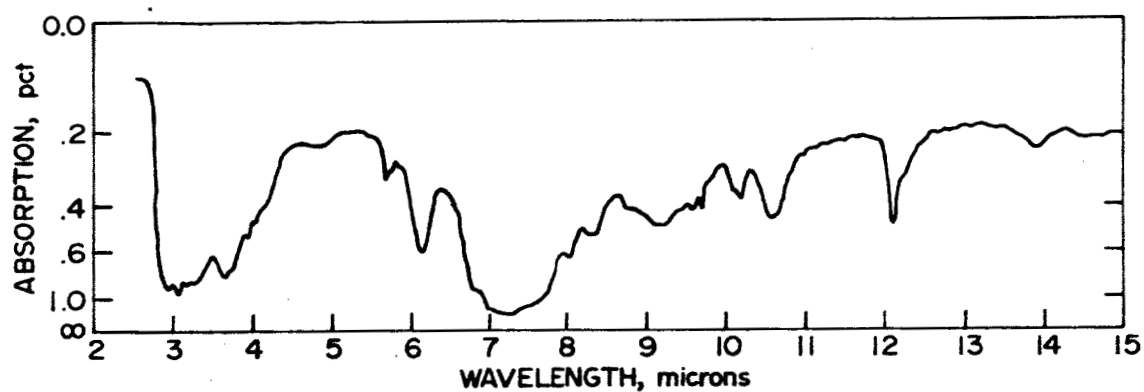
CHEMICAL REACTIONS OF THE HYPERGOLIC PROPELLANT COMBINATIONS

Introduction

In a previous section, the possible chemical reactions of the individual propellants were presented and evaluated with respect to the probability of their occurrence in the RCS engine. In light of the experimental results obtained with propellant combinations in the 2-D engine and in the flow reactor, it seems appropriate to discuss the reactions possible in the presence of combinations of these hypergolic propellants and concurrently to present available information of pertinent research.

Inevitably, the section describing reactions of the individual propellants touched on some of the secondary reactions of the combinations of the propellants; specifically, the reactions between the various fuels and nitrous acid.

Since there is an abundance of information in the literature, only that which is deemed most directly related to the hard-start problem is discussed.



DGM-73
719

FIGURE 29. - Infrared Spectrum of UDMH Preignition Residue Produced at -11°C by Reaction with NO_2 Vapor. (From Mayer, Taylor, and Schieler (82)).

Formation of Hydrogen Azide

Of all possible reactions, special attention has been given to the formation of azide in the N_2H_4/NO reaction, and its presence in our experimental reaction products.

Audrieth (88), in his book on hydrazine, cites early works of many researchers regarding the formation of hydrazoic acid from N_2H_4 . N_2H_4 and its derivatives react in the cold with nitrous acid to form hydrazoic acid (24).



Sommer and Pincas (89) have shown that the products formed from the reaction of N_2H_4 and HNO_2 depend on the pH of the solution.

In neutral solution:



In a strongly acidic solution:



If enough HNO_2 is present, the azide can further react with HNO_2 :



This reaction is faster than the previous one and is favored in excess acid.

These last few reactions indicate how critical the injection processes can be, in that a slight excess of oxidant favors formation of the azide. Even if excess oxidant is not intended, stream separation brings about changes in the initial O/F ratio and creates streams of varying O/F values. The results also suggest that a N_2H_4 lead may be beneficial in preventing an acidic reaction.

The nitrous acid necessary for the azide-forming reactions forms in the engine from the reaction of NO_2 and water according to the following reaction:



Although nitrous acid decomposes,

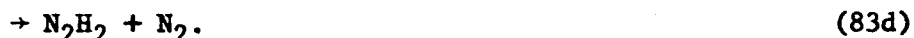


this latter reaction is comparatively slow in cold dilute solutions.

H₂O is found in the engine as a reaction product of the preignition reactions, while NO₂ is, of course, always found in equilibrium with N₂O:



The fact that N₃H and hydrazoic acid in aqueous solution are dangerous and extremely explosive has been known for a long time. Taylor (90) cites experiments by Joyner who measured the velocity of propagation of explosion in aqueous hydrazoic acid solutions. The results of Joyner's experiments--who lost his life while conducting the experiments--are summarized in table 4. These results show that this system detonates consistently when the HN₃ concentration exceeds 65 pct; aqueous solutions containing as little as 17 pct N₃H have also been known to explode. Azides, and N₃H in particular, undergo dissociation, decomposition, and explosive reaction, when irradiated (either electromagnetically or by nuclear particles). It was observed (91-92) for example, that when silver azide was irradiated in vacuo by ultraviolet light, an energy density of 8×10^{-4} cal/sq mm was sufficient to cause reaction. Moreover, if the amount of azide exceeded 0.2 to 1.5 mg, the theoretical amount of light required was independent of the mass of the azide; if a hot spot formed, explosion ensued. Photodecomposition of N₃H proceeds according to the steps:



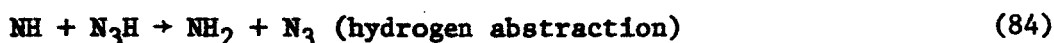
Certainly, enough illumination is released from the hypergolic reactions to initiate any azide present at the right concentration. Azide reacts with nitrous acid as shown in equation 80. Seel and Schwaebel (93) studied the same reaction and found strong evidence for the formation of an N₃-NO group, also reported by Clusius (94) and Stedman (95).

TABLE 4. - Velocity of propagation of explosions in hydrazoic acid solutions (aqueous)¹

Concentration of HN ₃ g/100 g solution	Normality of solution	Velocity, m/sec
80	22.1	8,500
70	18.0	7,300
67	17.2	7,100
65	16.8	1,700
61	15.7	630
60	15.4	384
54	13.8	233
48	12.2	40
38	9.8	2.5
30	7.3	1.0
16.7	4.0	.14

¹From J. Taylor (90)

Dows, Pimentel, and Whittle (96) observed the photolytic decomposition of N_3H and detected NH , N_2H_4 , and $(NH)_x$ ($x > 2$) among the products; although other schemes have been proposed, most of them include as the primary step hydrogen abstraction from N_3H . Spectroscopic studies of hydrazoic acid explosions suggest that in these systems (97) the NH formed is electronically excited. When HN_3 diluted with nitrogen is irradiated by a flash, only a small fraction (~ 10 pct) of the N_3H decomposes (98). In the absence of an inert gas, the energies absorbed from the flash and liberated in the subsequent reactions are enough to raise the temperature sufficiently for the N_3H to explode. Thrush (98) suggests the following mechanism for the photoreaction:



Gleu (99) analyzed the decomposition of aqueous solutions of N_3H by ultraviolet irradiation and detected, in addition to N_2 , hydroxylamine, small amounts of NH_3 , and traces of N_2H_4 .

Beckman and coworkers (100) measured the number of molecules of N_3H which decomposed per quanta of radiation absorbed and found a value of 2.9, which was largely independent of the pressure of the azide.

Azides also react with N_2O_4 and HNO_3 (18) according to the following:



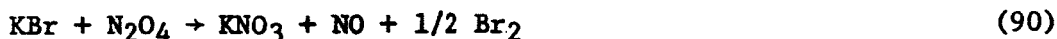
and



Nitrosyl azide, a very unstable compound, can form from azide by way of the next two reactions:



Because of the above, the chances of finding azides in the reaction products of NTO-rich runs are remote; furthermore, when KBr is used in the preparation of samples for analysis, it reacts with the NTO to form NO as follows:



so that NO can then react with any azide ion in the sample.

Pannetier and Lecamp (101) used an electric spark to decompose N_3H ; they established that explosive decomposition of the gas occurred only if the pressure of the azide exceeded a pressure limit of 5 mm Hg. Nitrogen, argon, and hydrogen were found to inhibit the explosive reaction; hydrogen being the most effective. When nitrogen was used as the diluent, ignition delays of the order of 1 to 2 seconds were observed at higher pressures; while at pressures slightly below the lower limit, a white deposit of unknown nature was seen in the chamber above the electrodes. The results of this study in which nitrogen and hydrogen show different degrees of inhibition, although both gases have essentially the same specific heat values, favor the hypothesis of a chain reaction in which NH_2 and NH radicals participate. The lower 5 mm Hg pressure limit for explosive decomposition is interesting in that it reminds one of Wasko's (102) observation--that explosions prevailed in N_2H_4 /NTO vapor phase reactions when the total pressure in the reaction vessel exceeded ~ 4 mm Hg.

Papazian (103) studied the photolysis of solid N_3H . To solidify N_3H , low temperatures are used; this slows the reactions and consequently it is possible to follow the kinetics of certain reactions which otherwise are too fast for observation with usual means of study. Explosions and detonations fall in this group; likewise, the decomposition of N_3H . The photolysis, or decomposition by irradiation, of N_3H indicated the possible formation of certain nitrogen chain compounds such as diiminohydrazine ($H-\ddot{N}=\ddot{N}-N=\ddot{N}-H$) and triazene ($H_2-N=N=N-H$). Papazian elaborates on the compounds and some of the related facts which partially substantiate these results, including the formation of N_2H and HN radicals which combine to form triazene; triazene in turn was found to decompose into ammonium azide (NH_4N_3).

In a later article, Papazian and Margozzi (104) refute the earlier results concerning the presence of triazene in the spectra of the products of photolysis of N_3H , and instead suggest water, whose spectrum is similar to that of triazene, as an intermediate. Attention has been focused on these two studies because of triazene, a precursor of an azide. Triazene is mentioned as one of the intermediates of the reaction between MMH and NTO in a series of studies by McLain (27).

In our experiments, we were especially careful to look for any evidence of azides either in the gaseous or condensed phase reaction products. Azide concentration in the gaseous products of the flow reactor's experiments, when present at all, was of insignificant quantity. The ability of the azide to adsorb on glass walls has been mentioned and may explain in part its absence in the gaseous products. Small azide peaks were noted in the infrared spectra of the condensed phase reaction products of both the 2-D engine and the flow reactor.

Weiss (105) studied the reaction between N_2H_4 and NTO at low temperatures and small amounts of azides are seen in the infrared spectra of the intermediates of the reaction. Ray and coworkers (73) reacted N_2H_4 and NTO

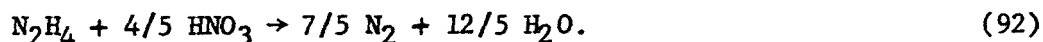
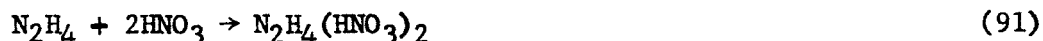
at low temperatures and found azide ions in the reaction products. Both reactants were greatly diluted with carbon tetrachloride; this dilution permitted the reaction to take place in the liquid phase without explosions or high pressure excursions. Unfortunately, carbon tetrachloride reacts with N_2H_4 to form triaminoguanidine and hydrochloric acid. The presence of the substituted guanidine and the hydrochloric acid may have an adverse effect on the main reaction mechanism, with the acid promoting azide formation.

Hypergolic Reactions With Nitric Acid as the Oxidant

Our major approach to the hard-start phenomenon, and that of a few other researchers, was based on the assumption that hard start might be caused by energetic chemicals accumulating in the engine to a concentration sufficient to initiate a strong explosion. The presence of liquid residues in test engines was suggestive, and the analysis of residues was helpful in offering a starting point for the investigation.

It is interesting to know that residues have been noticed earlier in tests of hypergolic propellant systems, similar to these in use in the RCS attitude control engines, and have drawn the attention of the investigators who detected them. And many have offered reaction mechanism schemes based on these residues. The research investigations mentioned in this section are all studies of hypergolic systems in which various concentrations of nitric acid were used as the oxidant.

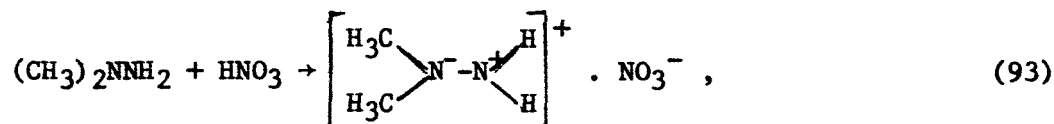
Bernard and Dufour (106) used a plexiglass engine which could withstand internal pressures of 145 atm, in their investigations with nitric acid and ethylenediamine. A residue recovered from the wall after an explosion was found to be ethylenediamine dinitrate. Solutions of the dinitrate in nitric acid were found to be even more heat sensitive than the salt itself. On the basis of their results, Bernard and Dufour (106) recommended the following mechanism for the nonflame and flame reactions of N_2H_4/HNO_3 , respectively:



Trent and Zucrow (107) studied the hypergolic reaction of dicyclopentadiene with white fuming nitric acid and they reported seeing a solid phase prior to ignition, and ignition propagating from the solid. The solid compound, some of which was recovered, when checked for shock sensitivity was found to be insensitive, but when rapidly heated it burst into flames. A few drops of concentrated nitric acid, when added to the solid, aided the combustion.

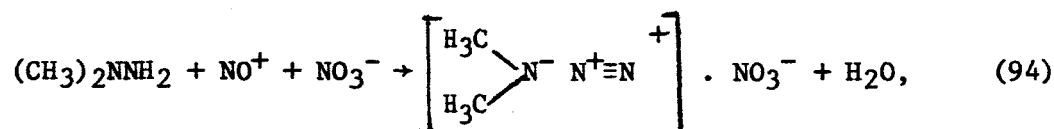
Spengler and Bauer (3) mixed UDMH with both nitric acid and with nitric acid fortified with NO_2 . Their results led them to offer the following reactions for the two systems.

Nitric acid system:

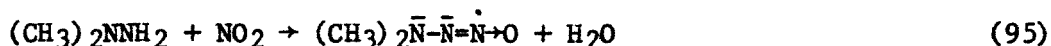


neutralization of a weakly basic amine group.

Nitric acid fortified with NO_2 :



or,



Summary and Conclusions

The Bureau's experimental program concerned with the chemistry of propellant systems in both a 2-D engine and a flow reactor is presented, together with a comparison of similar research by other investigators.

Gaseous products of reactions in these systems included oxides of nitrogen, hydrogen, oxygen, ammonia, and carbon monoxide and dioxide when the fuels were the substituted hydrazines.

The condensed phase products consisted mostly of water and nitrates; the nitrate formed was a function of the fuel and the O/F ratios. Only trace amounts of azides were found in a few of the condensed products.

More insight into the kinetics of the hypergolic reactions and the nature of intermediates formed could be gained by fast scanning spectroscopy. The nitrates, water, and the gases collected are the end products of the reactions.

A review of the overwhelming volume of published studies relating to the hard-start phenomenon reveals the complexity of the problem. Although more light has been shed on the problem, several more explanations have been found. Although nitrates, nitrites, dinitrates, azides, and other potential explosives have been shown to be present in the engine during preignition and post combustion periods, unfortunately, it was not possible to identify the specific compound(s) responsible for the destructive ignitions.

Thus, no single solution can be proposed to resolve the problem. But, in the present state of the art, it would appear that some generalities can be proposed.

Additives that should be evaluated in greater detail are these that reduce surface tension and thereby aid in the mixing of the propellants.

Additives that combine with water or that react with nitrous acid inhibit formation of N_3H , and thus are desirable. Promising materials are toluene, benzene, thiophene, and ethyl bromide, which were evaluated by Skinner, Hedley, and Snyder (12). Toluene and benzene are used in drying N_2H_4 in the process of preparing the anhydrous form. Thiophene undergoes nitration and nitrosation, i.e., it reacts with nitrous acid. Ethyl bromide reacts with N_2H_4 to form the mono and asymmetric diethyl hydrazine. Monoethyl hydrazine also offers possibilities of eliminating HNO_2 by reacting with it to form nitroso ethylhydrazine, $RN(NO)NH_2$.

Ethyl bromide as an additive is additionally attractive because it reacts with aldehydes, some of which are sensitive intermediates of the hypergolic reactions; specifically, formaldehyde (found in products of UDMH/NTO runs) is known to react explosively with NTO.

Koehler and his associates (67) suggest the addition of urea or of N_2O_5 . Urea was found to prevent formation of azide in UDMH/NTO systems. Urea's properties as an additive were studied by Lawver and Breen (43), who chose urea, among other additives, because of its ability to form NH_2 radicals, which take part in the decomposition scheme of N_2H_4 .

Another path in the prevention of azide formation can be the decomposition of N_2H_4 prior to its reaction with the oxidant. Hydrazine and hydrazine salts are decomposed by platinum to give nitrogen and ammonia. Although the rate of decomposition of hydrazine salts, such as the sulfate by platinum, is retarded by most inorganic acids, nitric acid enhances the rate (108). Nitric acid may also enhance the rate of decomposition of N_2H_4 .

Before any additive can be chosen, or for that matter before any definite solution is proposed, the cause of the problem has to be more narrowly defined.

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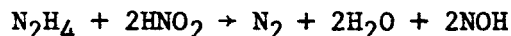
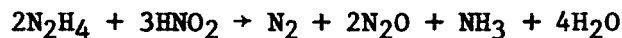
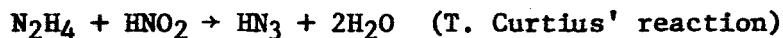
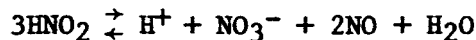
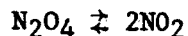
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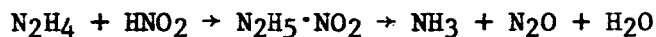
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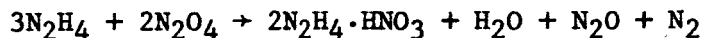
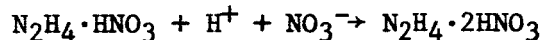
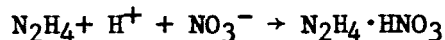
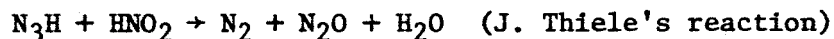
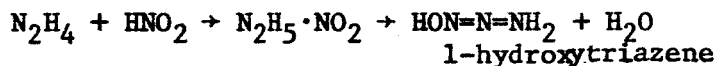
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APPENDIX A. POSSIBLE REACTIONS IN THE ENGINE¹I. $\text{N}_2\text{H}_4 + \text{N}_2\text{O}_4$ system (+ some water)

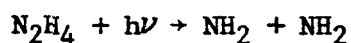
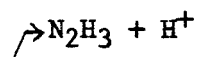
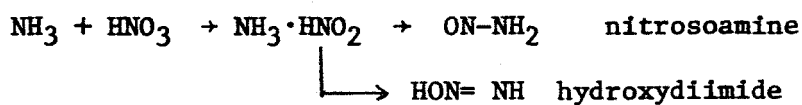
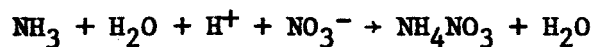
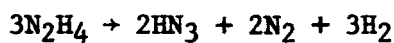
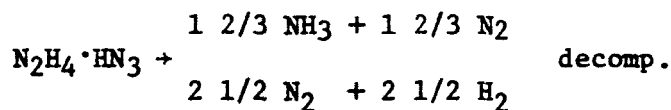
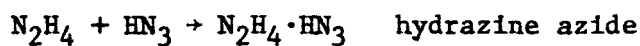
Nitrite



nitrosohydrazine



¹Compiled by the Bureau.



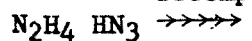
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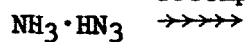
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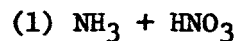
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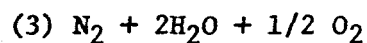
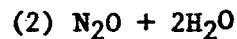


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APPENDIX B. KNOWN AND POSSIBLE SUBREACTIONS IN
THE HYDRAZINE-NITROGEN TETROXIDE REACTION¹

Reaction (all substances are taken as gases unless otherwise noted) ²		Heat of reaction at 25° C, kcal per g mol of first reactant in equation
N_2O_4	$\xrightleftharpoons{140^\circ} 2 \text{ NO}_2$	+13.9
$\text{N}_2\text{H}_4(\text{liquid}) + 2\text{NO}_2$	$\xrightarrow{<25^\circ} \text{N}_2\text{O} + \text{NH}_4\text{NO}_3(\text{sol.})$	-95.8
$\text{NH}_4\text{NO}_3(\text{solid})$	$\xrightarrow{400^\circ} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	-8.6
$\text{N}_2\text{H}_4(\text{liquid})$	$\xrightarrow{600^\circ} \text{NH}_3 + 1/2 \text{ N}_2 + 1/2 \text{ H}_2$	-23.0
NO_2	$\xrightarrow{920^\circ} \text{NO} + 1/2 \text{ O}_2$	+13.5
NO	$\xrightarrow{>1,350^\circ} 1/2 \text{ N}_2 + 1/2 \text{ O}_2$	-21.5
N_2O	$\xrightarrow{1,100^\circ} \text{N}_2 + 1/2 \text{ O}_2$	-19.6
$\text{N}_2\text{H}_4(\text{liquid}) + 2\text{N}_2\text{O}$	$\xrightarrow{760^\circ} 3\text{N}_2 + 2\text{H}_2\text{O}$	-166.8
$\text{NH}_3 + 3/2 \text{ N}_2\text{O}$	$\xrightarrow{950^\circ} 2\text{N}_2 + 3/2 \text{ H}_2\text{O}$	-105.1
$\text{H}_2 + \text{N}_2\text{O}$	$\xrightarrow{750^\circ} \text{N}_2 + \text{H}_2\text{O}$	-77.4
$\text{NH}_3 + 5/2 \text{ NO}$	$\longrightarrow 7/2 \text{ NO} + 3/2 \text{ H}_2\text{O}$	-15.4
$\text{H}_2 + \text{NO}_2$	$\xrightarrow{\sim 500^\circ} \text{NO} + \text{H}_2\text{O}$	-44.3
$\text{N}_2\text{H}_4(\text{liquid}) + 2\text{NO}$	$\longrightarrow 2\text{N}_2 + 2\text{H}_2\text{O}$	-170.6
$\text{NH}_3 + 3/2 \text{ NO}$	$\longrightarrow 5/4 \text{ N}_2 + 3/2 \text{ H}_2\text{O}$	-108.0
$\text{H}_2 + \text{NO}$	$\xrightarrow{>1,500^\circ} 1/2 \text{ N}_2 + \text{H}_2\text{O}$	-79.3
$\text{N}_2\text{H}_4(\text{liquid}) + \text{O}_2$	$\longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$	-127.7
$\text{NH}_3 + 3/4 \text{ O}_2$	$\xrightarrow{650^\circ} 1/2 \text{ N}_2 + 3/2 \text{ H}_2\text{O}$	-75.8
$\text{H}_2 + 1/2 \text{ O}_2$	$\xrightarrow{575^\circ} \text{H}_2\text{O}$	-57.8

¹Compiled by G. B. Skinner, W. H. Hedley, and A. D. Snyder (12).

²All temperatures in degrees centigrade.